A STUDY OF THE OXONIUM COMPLEX COMPOUND DIETHYL HYDRONIUM CHLORIDE

by

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B. Sc.

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A STUDY OF THE OXONIUM COMPLEX COMPOUND DIETHYL HYDRONIUM CHLORIDE

A DISSERTATION

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ABSTRACT

A STUDY OF THE OXONIUM COMPLEX COMPOUND DIETHYL HYDRONIUM CHLORIDE

A detailed investigation of the reactions between diethyl ether and hydrogen chloride has been carried out using vapour pressure measurements, by vacuum techniques. The study was made over a range of compositions between pure ether and equimolar amounts of ether and hydrogen chloride, and over the temperature interval from -18° to -98°C. Within these ranges, two complexes were investigated with the compositions: two molecules of ether per molecule of hydrogen chloride, and one molecule of ether per molecule of hydrogen chloride. Three equilibria were studied in detail. The first was the reaction of the components (2 ether and 1 hydrogen chloride) to produce the 2:1 complex. In this reaction ΔH was -3.37 kcal/mole and the entropy gain was 3.75 eu. (at -18°C). The second equilibrium studied was the conversion of the 2:1 complex to the 1:1 complex in the presence of hydrogen chloride for which a ΔH value of -1.09 kcal/mole and an entropy gain of 3.6 eu. at -18°C was found. The third equilibrium was that for the formation of the 1:1 complex directly from its components (ether and hydrogen chloride). This reaction was studied in the liquid phase and in dilute solution in n-heptane. It was found that for the reaction

ΔH = -2.25 kcal/mole in the liquid phase, and ΔH = -1.16 kcal/mole in the n-heptane solution. The corresponding entropy gains at -18°C were 3.8 and 16 eu. Comparison was made with the gas phase studies of Maass and Russel for the last equilibria. Attempts were made to explain the anomalous order of the ΔH values, and the nature of the interaction was discussed. It was concluded that further work is necessary if the problem of dielectric constant changes accompanying the formation of polar complexes in media of low dielectric constant is to be clarified. Further spectral studies are required on this system to evaluate the extent of charge transfer.

ACKNOWLEDGEMENT

It is a pleasure to acknowledge the valuable guidance and encouragement of Dr. W. J. Wallace, who directed this work.

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A STUDY OF THE OXONIUM COMPLEX COMPOUND

DIETHYL HYDRONIUM CHLORIDE

INTRODUCTION

Recently we have considered that the comparison of some properties of molecular complexes in the gas phase, the liquid phase, and in solution might offer a means of obtaining some information about solvation energies and the nature of specific solvent-solute interactions. It would be desirable, for such a study, to survey a system which is considerably dissociated, but which is stable enough for observation in convenient intervals of temperature and pressure.

Complexes between oxygen containing acceptor molecules and proton donor molecules (oxonium compounds) are suitable for such studies. Like their analogs in the nitrogen series, the ammonium compounds, the oxonium compounds are stable enough that reproducible studies of their properties can be made[1]. However, the degree of association and resultant compound polarity is much less in the oxygen series than in the more basic nitrogen series[2,3]. No free stable oxonium compound has yet been isolated[4].

The oxonium compound between diethyl ether and hydrogen chloride has been known for a long time[3,5]. Studies by Russel and Sullivan[1], and later by Buswell, Rodebush and Roy[2], indicated that despite the electrical

conductivity of the solutions, the complex was not dissociated into the free ions.

A study of ether cleavage reactions using hydrogen bromide[8] showed the strength of the ether oxygen--sliphatic substituent bond increases with increasing length of carbon chain, and that branched chains are more easily cleaved than straight chains, except where the branching is very close to the reaction site. The reported rate of the cleavage reaction, may parallel the activation energy required for the formation of the oxonium intermediate between the ether and hydrogen bromide. A comparative study using different hydrogen halides showed the reaction between dimethyl ether and hydrogen chloride to be rapid and homogeneous, while higher hydrogen halides reacted more slowly and heterogeneously[10].

Gas phase studies of ether-proton acid mixtures by Maass, Boomer and Russel[7,9], indicated marked interaction between components even at fairly elevated temperatures.

A number of investigators have shown that more than one compound is formed when an ether is mixed with a proton acid[5,11-17]. The complexes showing equimolar ratio between components were generally found to be the most stable species present. In many cases complexes containing more than one acid for each ether molecule

were sufficiently unstable that low temperatures were required for their study[13,18]. In those cases where the acid was highly undissociated (e.g. acetic acid), the complex was formed in the solid state or not at all[17,19,20]. This is an indication of the importance of having a loosely bound proton for interaction with oxygen. McIntosh[18] has studied the complexes with different molar ratios, and has found that the properties of the quimolar complex are markedly different from those in which the molar ratio differs from unity. This is probably an indication of a major difference between the basic structure of the equimolar compound and those of other molar ratios.

Spectral studies indicate a rather well defined disappearance of the acid proton vibrational frequency[21] and a lowering and deformation of the carbon-oxygen stretching frequency of the ether[22] as the two components are reacted. Raman studies indicate the appearance of the deformed hydrogen chloride rotation lines and a new band assigned to the marked deformation of the hydrogen chloride frequencies caused by the formation of higher order complexes[23]. On the basis of this evidence, the equimolar complex is formed by the acid proton becoming closely associated with the oxygen of the ether. The result is that the proton becomes bound to both the ether oxygen and to its own anion in the formation of the complex. When an excess of acid is present, higher

order complexes may form through the association of the excess acid with the anion end of the oxonium complex dipole.

THE EXPERIMENTAL PART

I - PREPARATION OF MATERIALS

Diethyl Ether: The diethyl ether was purified in the following manner. Ether (Merck Reagent Grade, Anhydrous) was refluxed over calcium hydride for twenty-four hours, and was then distilled through an Illinois column fitted with ground glass joints, into a flask containing fresh calcium hydride. The first and last fractions of ten percent were discarded. The center fraction was then distilled through a 130 cm. long adiabatic distilling column packed with glass Raschig rings, fitted with a fractionating head which gave a reflux ratio of about 15:1 by means of dividing capillary outlet tubes. The center fraction of 100 ml. was collected in a 200 ml. flask fitted with a ₸ 24/40 ground glass joint and containing a small amount of calcium hydride to remove any last traces of peroxide or moisture. The flask containing the purified material was immediately attached to the vacuum line by means of a ₸ 24/40 to ₸ 15/30 adapter joint. The sample was frozen with liquid nitrogen and the apparatus evacuated. Once a suitable vacuum had been obtained, the sample was allowed to warm up to room temperature whence it was transferred into a U tube in the line, cooled by liquid nitrogen, with continuous pumping to remove dissolved gases from the ether. Further degassing was achieved by melting the sample,

warming it to room temperature, and refreezing it as before with further pumping. When this operation had been repeated two more times, the sample was taken to the fractionation system for further purification. The U tube containing the ether was immersed in a Dewar flask containing a solution of Dry Ice in alcohol (-80°C). A Dewar flask containing liquid nitrogen (-195°C) was placed around the next U tube in the fractionation train to form a cold trap. The interconnecting Stock valve was then opened and the sample was allowed to vapourize from the -80° bath into the cold trap. After about ten percent of the sample had transferred, the Stock valve between the two U tubes was closed, and the U tube containing the residual fraction of ether was isolated from the rest of the system while the vapourized material was taken out of the line and discarded. After this operation had been completed, the system was re-evacuated and the Stock valve isolating the first U tube from the rest of the system was reopened. The evaporation process was then allowed to continue u until the residue was only ten percent of the original. This residue, like the original fore-run, was discarded after isolation. The middle fraction was re-fractionated two more times using the same method. The vapour pressure of the accepted ether fraction was measured at -23.5°C (Table I) as small amounts of ether were dis-

tilled away. The presence of any appreciable amounts of impurity would be noticed here by a change in vapour pressure from fraction to fraction. This is a very sensitive test for minute amounts of volatile impurity. A sample exhibiting the same vapour pressure for all its fractions is said to be tensimetrically homogeneous. Once the ether had been established to be tensimetrically homogeneous, it was transferred to another part of the line for storage. The stored ether was analysed with a Fisher-Gulf gas chromatotagraphy unit and the sample was shown to be free of any impurities (Fig. 7).

Hydrogen Chloride: Two methods of preparation of hydrogen chloride were used in these experiments. The first utlized the fact that anhydrous aluminum chloride when stored for long periods of time absorbs moisture. If this salt is heated gently, hydrolysis occurs with the liberation of hydrogen chloride. For our purpose several bottles of aluminum chloride (May and Baker Anhydrous) were available. A sample of this salt was intorduced into an apparatus (Fig. 1) which consisted of a 100 ml. bulb (a) above which was fitted a plug of glass wool (b) and a second 100 ml. bulb (c) which was filled with silica gel to prevent further moisture from entering the reaction bulb. Above this second bulb was a ₸ 15/30 ground glass joint (d). This apparatus was connected to the vacuum line and evacuated. It now was

possible to generate gaseous hydrogen chloride by carefully heating the aluminum chloride. The generator was heated until the vacuum line contained about 0.5 atm. of gas. The generator was then closed off from the line, by a stop cock, and purification of the hydrogen chloride was begun.

Due to difficulties in controlling the dry type generator, a second method of preparing hydrogen chloride was used for subsequent additions of gas to the line. A generator (Fig. 2.) was constructed consisting of a 100 ml. dropping funnel (a) fused into a 200 ml. reaction vessel (b) onto which was connected an inlet for addition of solid reactants (c), and an outlet tube (d) leading into a special U tube (e). The U tube was fitted with an inlet tube (f) for adding solid drying compounds, and an outlet tube (g) fitted with a stopcock (h) and a ₸ 15/30 joint (j) for connection to the vacuum line. Potassium chloride (May and Baker Reagent) was introduced into the reaction vessel (b), concentrated sulphuric acid, (C.I.L.) was poured into the dropping funnel (a) and phosphorus pentoxide (Merck Reagent) was introduced into the special U tube (e). The generator was then connected to the vacuum line and evacuated. An alcohol-Dry Ice bath was then placed on the first U tube of the vacuum line, in order that any moisture passing through the drying tube (e) of the generator would be condensed away from the

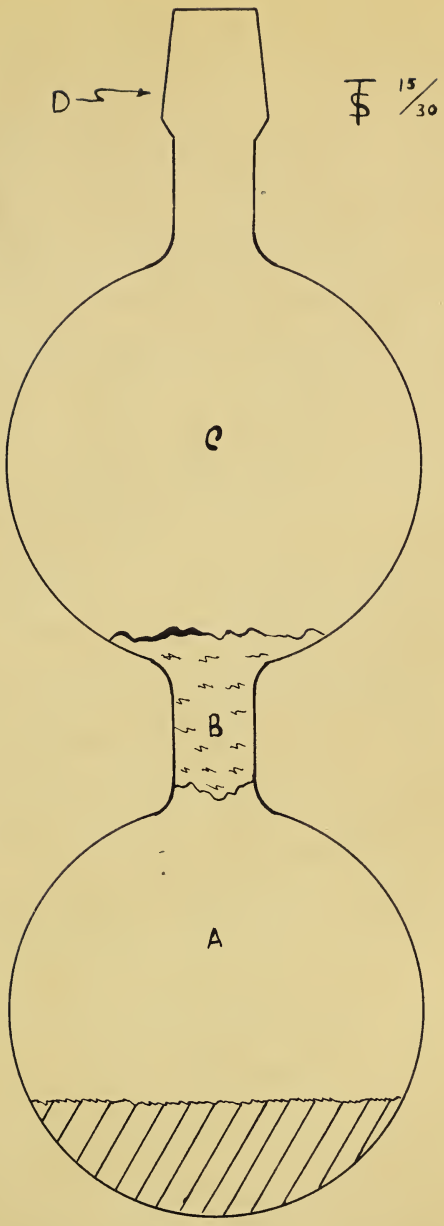

Figure 1. Hydrogen Chloride Generator - Dry Method

hydrogen chloride. The generator was then started by allowing a small amount of the sulphuric acid to fall from the dropping funnel (a) on the potassium chloride. Generation was continued until the vacuum line contained about 0.5 atm. of gas. The generator was then closed off from the line by closing the stopcock (h), and the purification of the hydrogen chloride was then begun.

The hydrogen chloride was treated by fractionation to remove traces of residual moisture and other less volatile impurities. This was accomplished by freezing the entire gas sample in the first U tube of the fractionation section of the vacuum line with liquid nitrogen. The frozen sample was isolated from the rest of the system, while the line was pumped out to remove any non-condensible gases. At this time, a Dry-Ice-alcohol bath was placed on the U tube containing the frozen sample and a liquid nitrogen bath on the second U tube of the fractionation train. The Stock Valve between the two U tubes was then opened and the hydrogen chloride was allowed to sublime with continuous pumping into the liquid nitrogen trap. When most of the sample had passed over, the Stock valve was closed and the frozen sublimate isolated from the rest of the line while the residue was removed from the system. This residue contained most of the remaining non-volatile impurities which were originally present in the sample, but to be sure that all

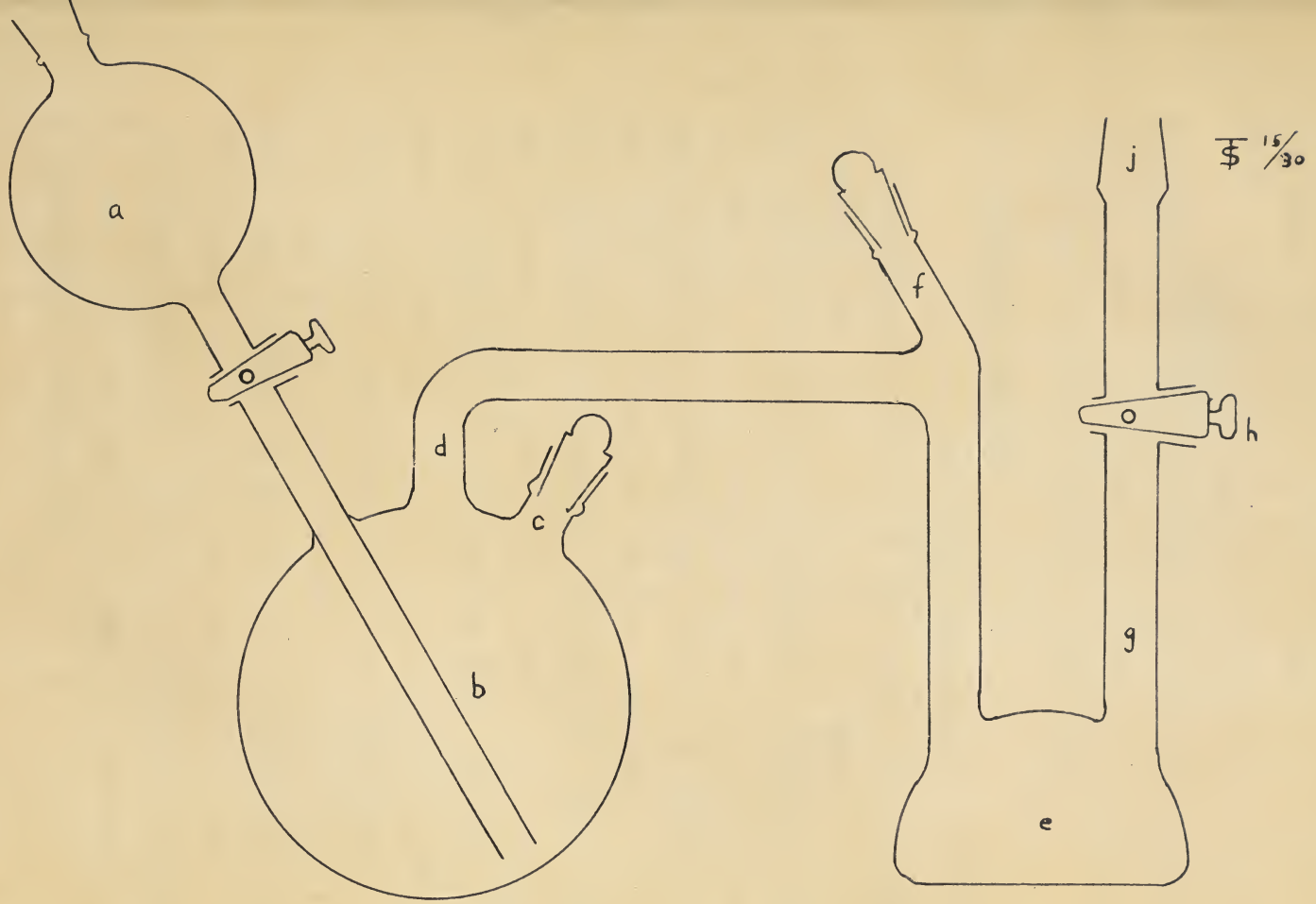

Figure 2. Hydrogen Chloride Generator - Wet Method

were totally removed, the process was repeated four more times. Once this had been done, the hydrogen chloride was transferred into a suitable gas storage vessel.

n-Heptane: n-Heptane (Eastman white label) was dried with calcium hydride and distilled, introduced into the line, fractionated and tested for tensimetric homogeneity in similar fashion to the ether.

II - ANALYTICAL METHODS

Liquid samples (ether and heptane) were taken by transferring a portion of the liquid from storage to a weighing tube (Fig. 3). The total weight of sample was known from weighing by difference, assuming complete transfer from the tube back into the line after weighing. The efficiency of transfer was checked by weighing the tube before and after the sampling operation. With care, good agreement was obtained. (Tables III, IV). Gaseous samples were measured out using a measuring bulb of known volume connected to a mercury manometer (Fig. 5). The amount of sample was calculated from the Ideal Gas Laws, using the bulb temperature (i.e: the temperature of the room), the measured pressure and the known volume of the bulb. The accuracy of the results obtained were checked by measuring the variation of pressure of a sample with temperature (Table V). The error in quantity measured was shown to be negligible compared to the reading errors in pressure and temperature.

III - THE VACUUM LINE

The experiments described in this work were performed in a Stock type vacuum apparatus described by Sanderson[24]. When the techniques used were peculiar to this type of apparatus, their description is not repeated here. H wever, where modified or new techniques are used, they will be described with the experiments where their application was made.

IV - DETERMINATION OF THE VAPOUR PRESSURE-COMPOSITION CURVE IN THE LIQUID PHASE:

The variation of vapour pressure of a solution as a function of composition is relatively easy to measure. The components are mixed in known proportions and the solution is allowed to equilibrate at constant temperature. Once the equilibrium is attained, the vapor pressure of the system is measured.

To determine the shape of the curve, solutions of various proportions were prepared using a fixed sample of ether and adding hydrogen chloride in small portions. The size of the ether sample chosen was determined by the composition range under study. For convenience, the size of the hydrogen chloride additions were kept close to one or two milli-moles. For study of solutions of low mole-ratio in hydrogen chloride, larger ether samples were used than for studies nearer to equimolarity.

The apparatus shown in Fig. 4 was assembled and thoroughly degassed. Degassing is the process of

desorbing stubbornly held adsorbates from the walls of the glass reaction system. Most of the surface gases are removed by heating the highly evacuated system (10^{-5} mm. Hg) with an air-gas flame until the yellow color of the sodium flame appeared. In this process one or two flamings were sufficient to satisfactorily degass the system. The glass surface is heated to incipient fusion, and the clean glass surface produced is not readily recontaminated.

A weighed sample of diethyl ether was introduced into the reaction bulb (A) from the weighing tube, using a bath of liquid nitrogen around the reaction bulb for the transfer. When total transfer had occurred, the Stock valve (B) was closed isolating the reaction system from the rest of the vacuum line. The reaction bulb was then immersed in a Dry-Ice-alcohol bath, and the ether was allowed to come to equilibrium with occasional stirring, using the magnetic stirring rod (C) operated by two large horse-shoe magnets. The vapour pressure of the sample was measured on the measuring manometer (D), using a Cathetometer (Gaertner M-911).

The cold bath itself was found to be most efficient, if a finely ground slush of Dry Ice in alcohol was used in a one quart Dewar flask. As long as Dry Ice remained in solution, the constant temperature of sublimation was maintained. Using such a large Dewar, it

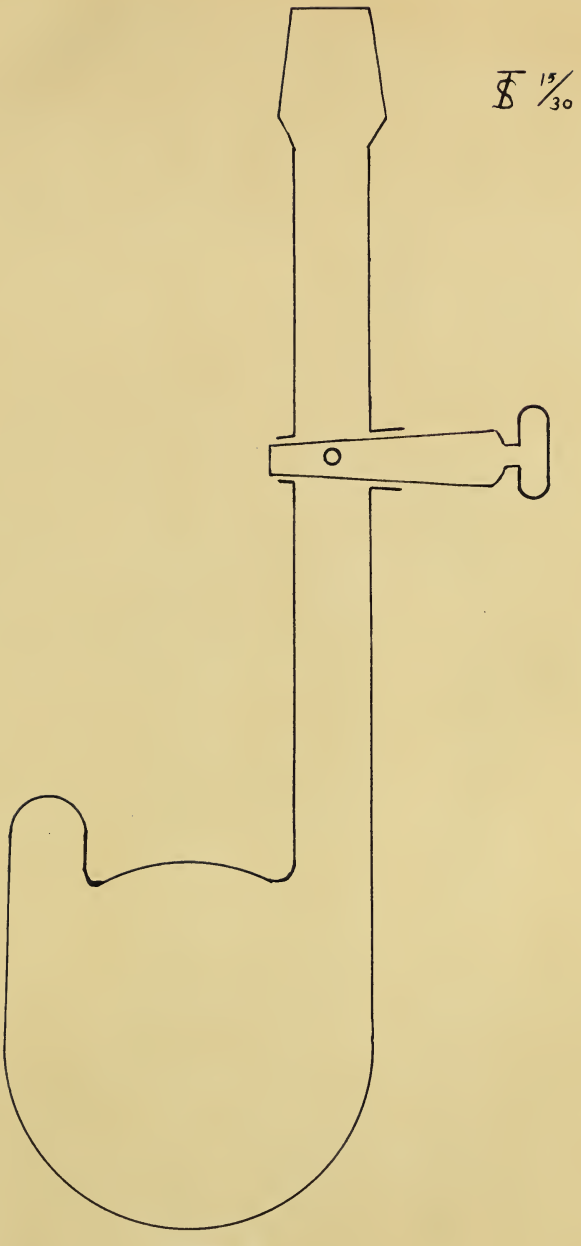

Figure 3. Weighing Tube

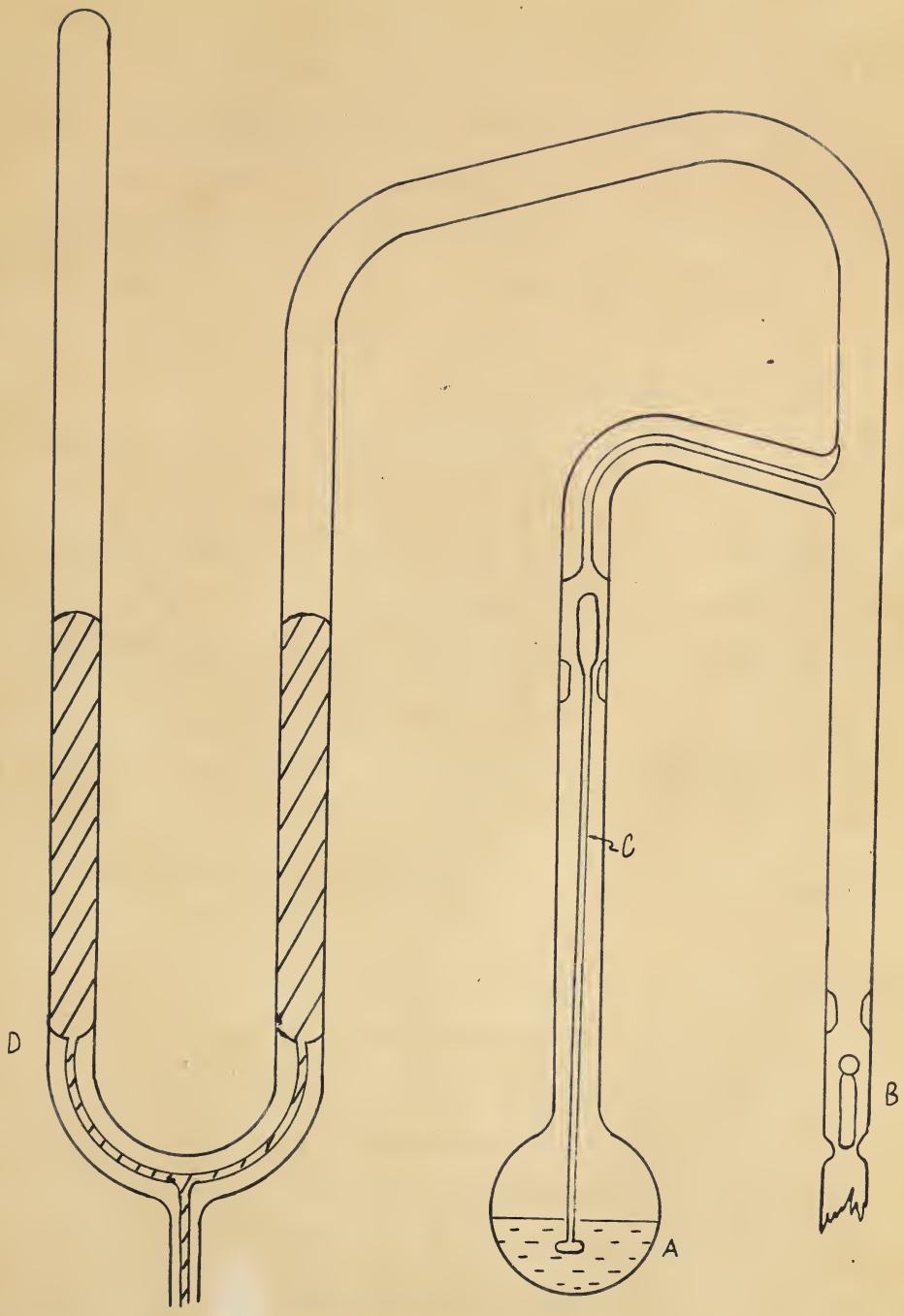

Figure 4. Pressure Measuring System

was found that the temperature could be maintained within 0.1°C for 8 hours and to within 0.25°C for two days. Temperatures were measured using an Iron-Constantan themocouple (0°C warm junction) connected to a Leeds-Northrop Student Model Potentiometer. When the vapour pressure had been measured, a sample of hydrogen chloride was measured out in preparation for introduction into the measuring system.

A convenient method for measuring out gas samples utlizing a gas measuring bulb (Fig. 5) was used. The bulb was calibrated by weighing the water it contained. Before connection to the vacuum line, the bulb was filled with cooled, boiled distilled water to the mark (B) and weighed. From the weight of the dry bulb, the weight of the water and volume of the bulb were readily calculated. In operation, the mercury in the right hand side of the constant level manometer, was always adjusted to the mark (B), hence the volume of the bulb was always the calibrated value.

In using the bulb to measure out gas samples, a small amount of gas was transferred into the bulb and frozen with liquid nitrogen. The mercury was then allowed to flow into the manometer, by opening the stopcock (A) connecting the manometer with its mercury reservoir, until the level of mercury was above the mark (B). All uncondensed hydrogen chloride in the line

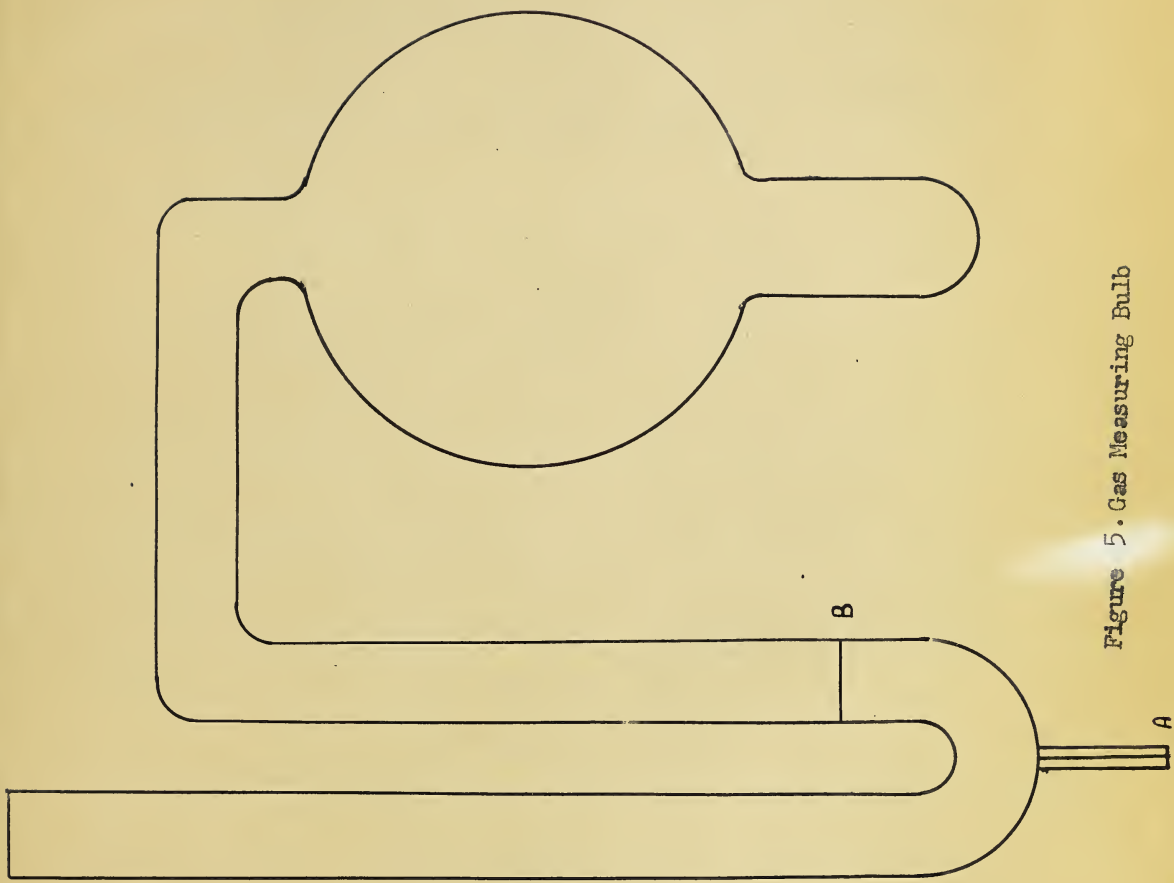

Figure 5. Gas Measuring Bulb

was then transferred back into storage using a nitrogen bath on the storage bulb. The sample in the standard bulb was then allowed to warm up to room temperature, at which time the mercury in the manometer was adjusted exactly to the mark (B), and the pressure of the sample read on the manometer. The amount of sample could then be calculated, assuming the Ideal Gas Law to be valid for the sample.

The measured sample in the standard bulb was then frozen using liquid nitrogen. The ether in the reaction system was them similarly cooled, and when both samples were thoroughly frozen, the interconnecting Stock valve and manometer were opened and transfer was allowed to occur from the standard bulb to the reaction bulb. By removal of the liquid nitrogen bath the frozen hydrogen chloride was warmed to room temperature, promoting sublimation of the hydrogen chloride into the ether.

When all the measured hydrogen chloride had been transferred into the ether, the Stock valve (B) was closed, and the liquid nitrogen bath was again replaced by a Dry-Ice-alcohol bath. The mixture was then allowed to equilibrate with occasional stirring before its vapour pressure was measured.

After the completion of this operation, more hydrogen chloride was added and another vapour pressure reading was taken. This process was continued until

readings of the vapour pressure of various diethyl ether-hydrogen chloride solutions of convenient composition had been recorded. At this time the total sample in the reaction bulb (A) was discarded,and a new smaller ether sample weighed out for further readings.

V - DETERMINATION OF THE VAPOUR PRESSURE-TEMPERATURE CURVE IN THE LIQUID PHASE

The variation in vapour pressure of a solution of known composition as a function of temperature can be measured rather conveniently. The components are again mixed in known proportions, and the solution is allowed to come to equilibrium at the desired temperature with occasional stirring. Once reached, the equilibrium pressure is again measured. To determine the exact curve, the vapour pressure of each solution was measured at several temperatures, using melting baths of purified liquid reagents. The temperature range under study was from -17°C to -100°C. The higher temperature melting baths (o-dichloro benzene (-17.6°C) and chloro benzene (-45.2°C) were longer lasting (4 to 5 hours) than the lowest melting bath (methanol (-97.8°C)), which only lasted 2 hours. The Dry Ice-alcohol bath was used as the standard comparison temperature for the work.

VI - DETERMINATION OF THE VAPOUR PRESSURE OF THE 1:1 COMPLEX IN AN INERT SOLVENT

The effect of an inert solvent on the equilibrium betweem ether and hydrogen chloride was investigated. In

order to accomplish this, a weighed sample of n-heptane, purified as indicated previously, was introduced into the vacuum line. A small weighed sample of ether was then introduced into the n-heptane to form a dilute solution of ether in heptane. A hydrogen chloride sample was measured out, of sufficient size to bring the solution to a point just a little below equimolarity with respect to the ratio of hydrogen chloride to ether. This measured sample was then introduced into the ether-heptane solution, and the resultant pressure was measured. Small additions of hydrogen chloride were then made to bring the solution first up to, and then slightly past equimolarity. The resultant pressures were taken after each addition. In the study, the relative sizes of the ether and hydrogen chloride samples were chosen such that when subsequent additions of hydrogen chloride were made to the solution, the effective concentration of dissolved species in solution was not altered appreciably. Readings were carried out of the vapour pressures at the various compositions, at two temperatures (-18.4 and -76.7°C).

RESULTS

PURIFICATION OF MATERIALS

Diethyl Ether: The diethyl ether was tested (-23.5°C) and found to be tensimetrically homogeneous.

TABLE I

Test of Purified Diethyl Ether

Vapour Pressure of Sample	55.15 ± 0.05 mm.
Vapour Pressure of Distillate	55.15 ± 0.05 mm.
Vapour Pressure of Residue	55.15 ± 0.10 mm.
Temperature[1]	-23.5 ± 0.10 °C.

[1] Temperatures measured using a Leads-Northrop Student Model Potentiometer and an iron-constantan thermocouple with an ice (0.0°C) reference junction.

The vapour pressure of the accepted ether sample was determined at various temperatures. The results are shown in Table II and are plotted in Fig. 6.

TABLE II

Vapour Pressure - Temperature Data for Ether

T(°K)	$1/T \times 10^{-3}$	P(mm. Hg)	$\log_{10} P$
273.1	3.662	186.2	2.2700
249.7	4.004	55.15	1.7416
227.9	4.387	13.65	1.1351
194.2	5.150	0.70	1.8451

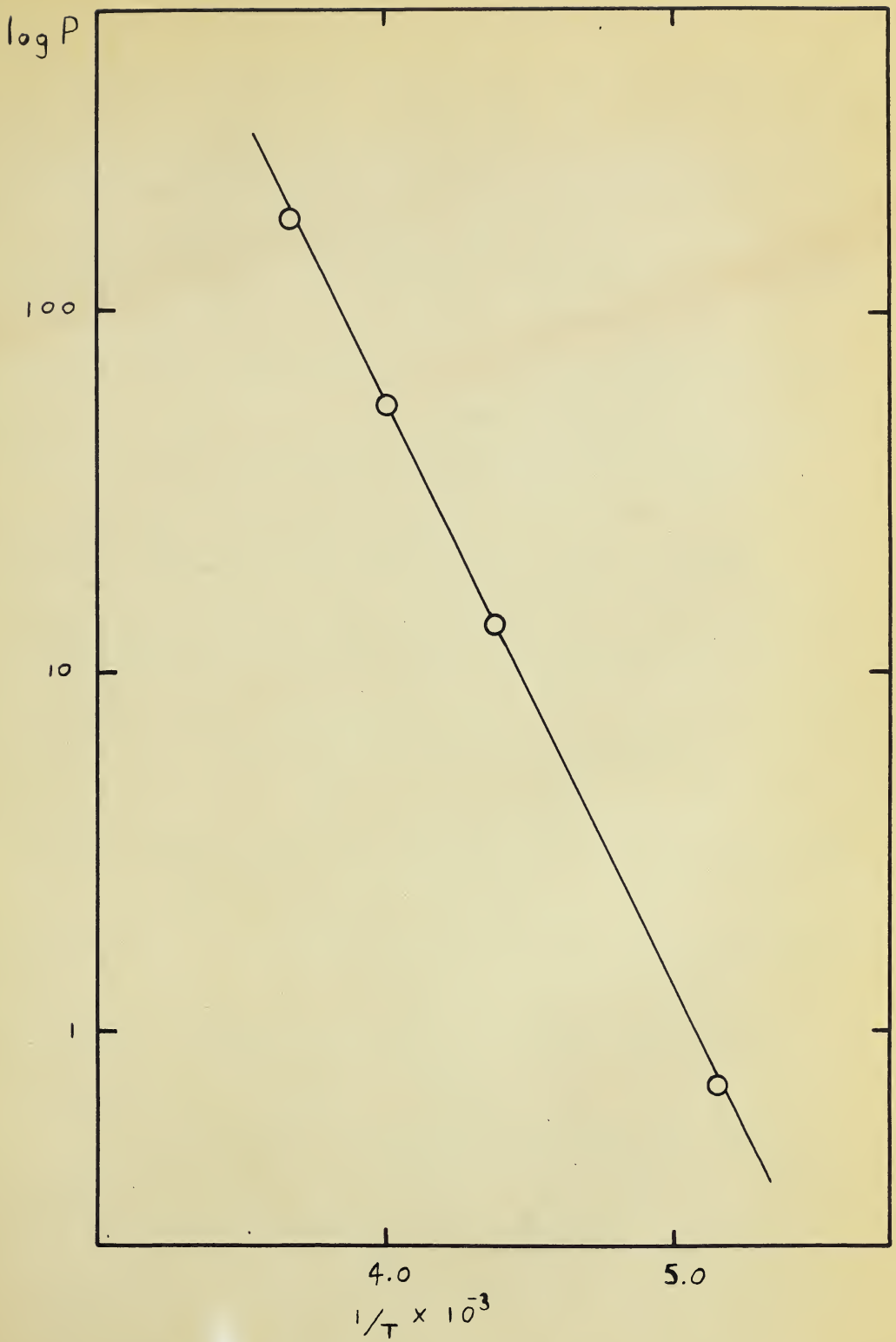

Figure 6 Plot of Log P vs 1/T for Ether

Gas chromatograms were run on a purified and on an unpurified ether sample, the results are shown in Fig. 7. These results, coupled with the vapour pressure tests showed the ether to be free of volatile impurities.

Hydrogen Chloride: The prepared samples of hydrogen chloride were assumed to be free of interfering impurities after their fractional distillation in the vacuum line. This assumption of purity can be justified when the magnitude of differences in properties between the hydrogen chloride and those impurities probably present in the generated sample (i.e: Method One - water, aluminum oxide; Method Two - water, sulphur dioxide, sulphuric acid) is considered. In all cases excepting those in which severe contamination of the prepared sample might occur, the separation process used, would yield essentially quantitative separation of generated hydrogen chloride from impurities. In cases where contamination was suspected, the entire sample was rejected and a fresh supply of hydrogen chloride was generated. In this way, it is doubtful if any measurable error is introduced into the results by not testing the hydrogen chloride for volatile or other interfering impurity before using.

n-Heptane: The samples of n-Heptane were fractionated until a qualitative test showed the sample to be roughly tensimetrically homogeneous. Since the n-Heptane was only used as an inert solvent (in a region

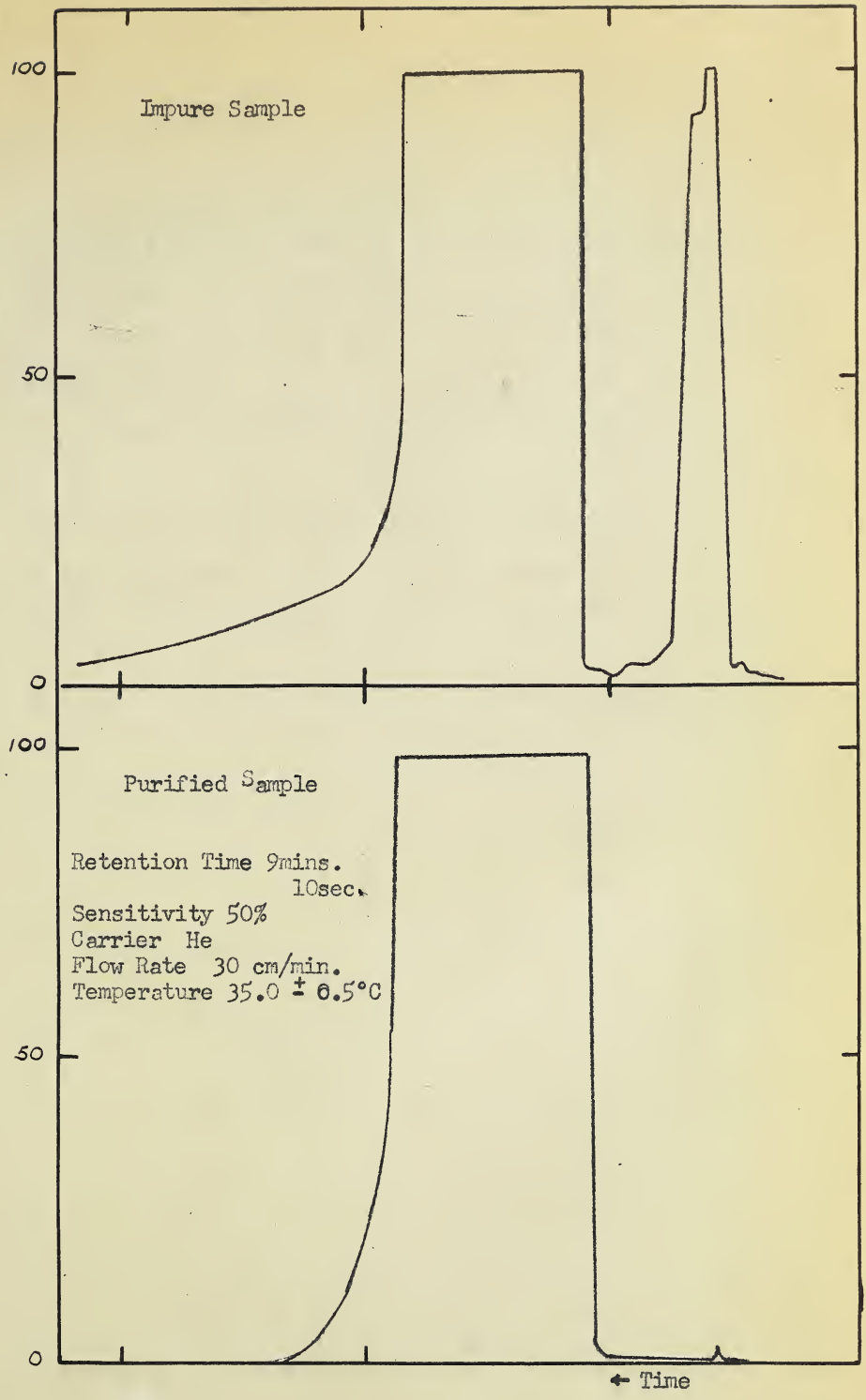

Figure 7 Gas Chromatograms for Ether

where its vapour pressure was negligible compared to the system being studied), the error introduced by small deviations from tensimetric homogeneity would not be large enough to affect the validity of the results obtained.

ANALYTICAL METHODS

Introduction of Liquid Samples: The actual process of transfer of a liquid sample from the weighing tube must be attached to the vacuum line by way of a greased ground glass joint, meticulous care must be taken before the weighing operation in removing all of the grease from this ground glass joint. It was found that despite the care taken to be sure that the grease had been completely removed from the sample tube, the error introduced into the weighing because of incomplete removal was measurable in most cases. Typical deviations are shown in Table III, taken from sugsequent weighings of a sample tube during the sampling operation, the tube being thoroughly wiped with a clean cloth moistened with carbon tetrachloride between weighings.

Table III

Error from Grease on Sample Tube

Initial Weight	Subsequent Weight	Deviation
83.3894	83.3896	+0.2 mg.
83.5666	83.5664	-0.2 mg.
83.5785	83.5782	-0.3 mg.
83.3715	83.3719	+0.4 mg.
86.6529	86.6526	-0.3 mg.

Average Deviation $\pm$ 0.3 mg. per weighing

In order to determine if the total sampling error was in degreasing the weighing tube, or if any ether was lost in the actual transfer into the vacuum line, a weighed sample of ether was introduced into the line and then removed for reweighing. The result is given in Table IV.

Table IV

Efficiency of Liquid Transfer

Weight of Original Ether Sample	0.8819 $\pm$ 0.0003 gm.
Weight of Removed Ether Sample	0.8825 $\pm$ 0.0003 gm.
Average weight of Ether Sample	0.8822 $\pm$ 0.0003 gm.

From the results of these tests on liquid sampling, it is doubtful that any of the error comes from the actual transferring process itself, but more likely that most of the error results from the cleaning process

before weighing. However, if care is taken, the error in weight can be kept below 0.5 mg., which would only introduce an uncertainty of about 0.25% in the weight of the average ether sample used.

Calibration and Use of the Gas Measuring Bulb

The standard gas measuring bulb (Fig. 5) was calibrated by filling it with distilled water and weighing it. From this the volume of the bulb could be calculated.

Weight of Water in bulb	540.0 $\pm$ 0.1 gm.
Temperature of Water	25.0 $\pm$ 0.1° C.
Weight of 1 ml. of Water (at 25.0°C)	1.00294 gm.
Volume of Bulb = V_o	542.1 $\pm$ 0.3 ml.

The amount of the gas in the bulb at any time could be found using the Ideal Gas Law, if the pressure and temperature of the gas are known.

$$P V_o = n R T$$

where P is the measured gas pressure (mm. Hg)

V_o is the volume of the bulb (ml.)

T is the temperature of the gas (°K)

and R is the universal gas constant (ml., mm./deg.,mole).

However, it was found more convenient to use a comparative measurement using the Ideal Gas Laws in the following form.

$$\frac{P_o V_o}{n_o T_o} = \frac{P V}{n T}$$

Where P is one atmosphere

V is the volume of 1 mole of gas at S.T.P. (22.41.)

T is 0°C (273.1° K)

and n is one mole of gas,

and where n_o is the required gas sample of 1 mole

P_o is the pressure of this sample in the bulb

V_o is the volume of the bulb

and T_o is the temperature of the gas sample during measurement.

From this relationship, the following was obtained for the pressure of a one millimole gas sample in the measuring bulb at T °K.

$$P = \frac{760 \times 22{,}400 \times T}{542.1 \times 273.1 \times 1000}$$

A table of values of P over a range of T values was prepared and the quantity of the gas sample measured was found using the following relationship:

$$\frac{Po}{N_o \ T_o} = \frac{P}{n \ T}$$

where the subscripts ($_o$) refer to standardized conditions, and the other values are the measured con-

conditions.

So we get $$n = \frac{P \quad N_o}{P_o} = \frac{P}{P_o}$$

Utilizing this relationship, measurement of gas samples could be obtained to 0.8 % so that for most measurements made in the study, the accuracy per millimole of measured gas was within $\pm$ 0.008 moles. An actual check was made on this accuracy, by measuring the pressure of a single gas sample at different temperatures, the results are tabulated in Table V.

Table V

Pressure-Temperature Variation of a Gas Sample

P (mm.)	T(°K)	Sample (mmoles)	Deviation (mmoles)
9.9	299.6	0.287	-0.004
10.0	299.3	0.291	0.000
10.2	298.5	0.297	+0.006

DETERMINATION OF THE VAPOUR PRESSURE COMPOSITION DIAGRAM AT -78.9°C

The vapour pressure of a weighed ether sample was measured at -78.9°C and its change was recorded as measured amounts of hydrogen chloride gas were added to it. The various data observed are given in Tables VI and VII and these data are plotted in Figures 8 and 9.

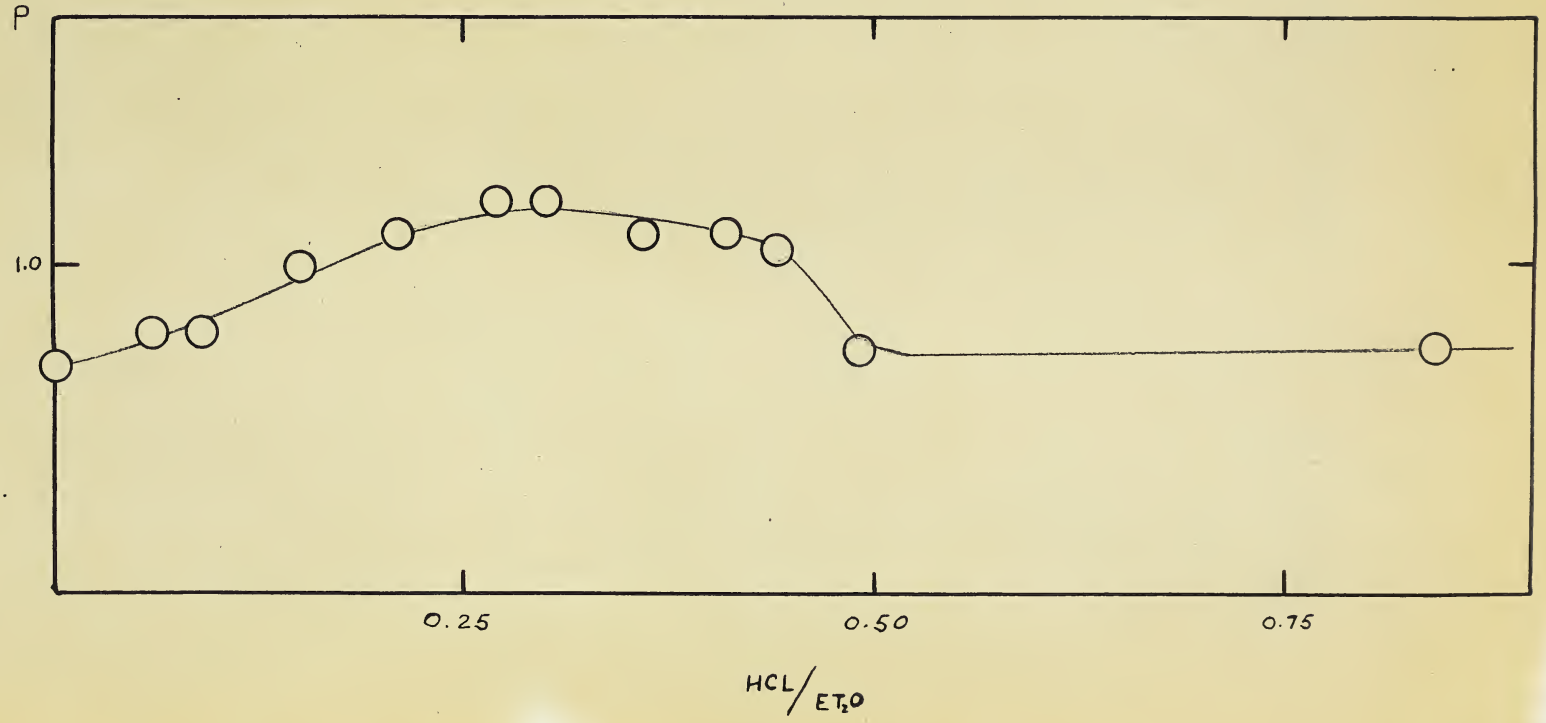

Figure 8 Vapour Pressure - Composition Diagram (at -78.9°C)

TABLE VI

Vapour Pressure - Composition Data at -78.9°C

(Et_2O = 32.3 mmoles)

HCl (mmoles)	P (mm.)	$\frac{HCl\ (mmoles)}{Et_2O\ (mmoles)}$
0.00	0.70	0.00
1.99	0.80	0.06
2.98	0.80	0.09
4.99	1.00	0.15
6.78	1.10	0.21
8.68	1.20	0.27
9.64	1.20	0.30
11.6	1.10	0.36
13.3	1.10	0.41
14.3	1.05	0.44
3.14	0.75	0.49[1]
4.02	0.75	0.84[2]

[1] Et_2O = 6.41 mmoles

[2] Et_2O = 4.79 mmoles

Table VII

Vapour Pressure - Composition Data at -78.9°C

(Et_2O = 8.11 mmoles)

HCl (mmoles)	P (mm.)	$\frac{HCl\ (mmoles)}{Et_2O\ (mmoles)}$
4.08	0.70	0.50
5.01	0.70	0.62
5.96	0.75	0.74
6.88	0.80	0.85
7.48	1.05	0.92
8.13	1.55	1.00
9.05	2.80	1.12
9.98	4.15	1.23

DETERMINATION OF THE VAPOUR PRESSURE-TEMPERATURE-COMPOSITION DIAGRAM

Further studies were carried on as before of the vapour pressure of a weighed ether sample, as measured amounts of hydrogen chloride were added to it. This time, vapour pressure readings were taken at a variety of temperatures for each composition. The temperatures used were obtained using the freezing or subliming substances given in Table VIII. The observed data are recorded in Table IX and are plotted in Figures 10, 11, and 12.

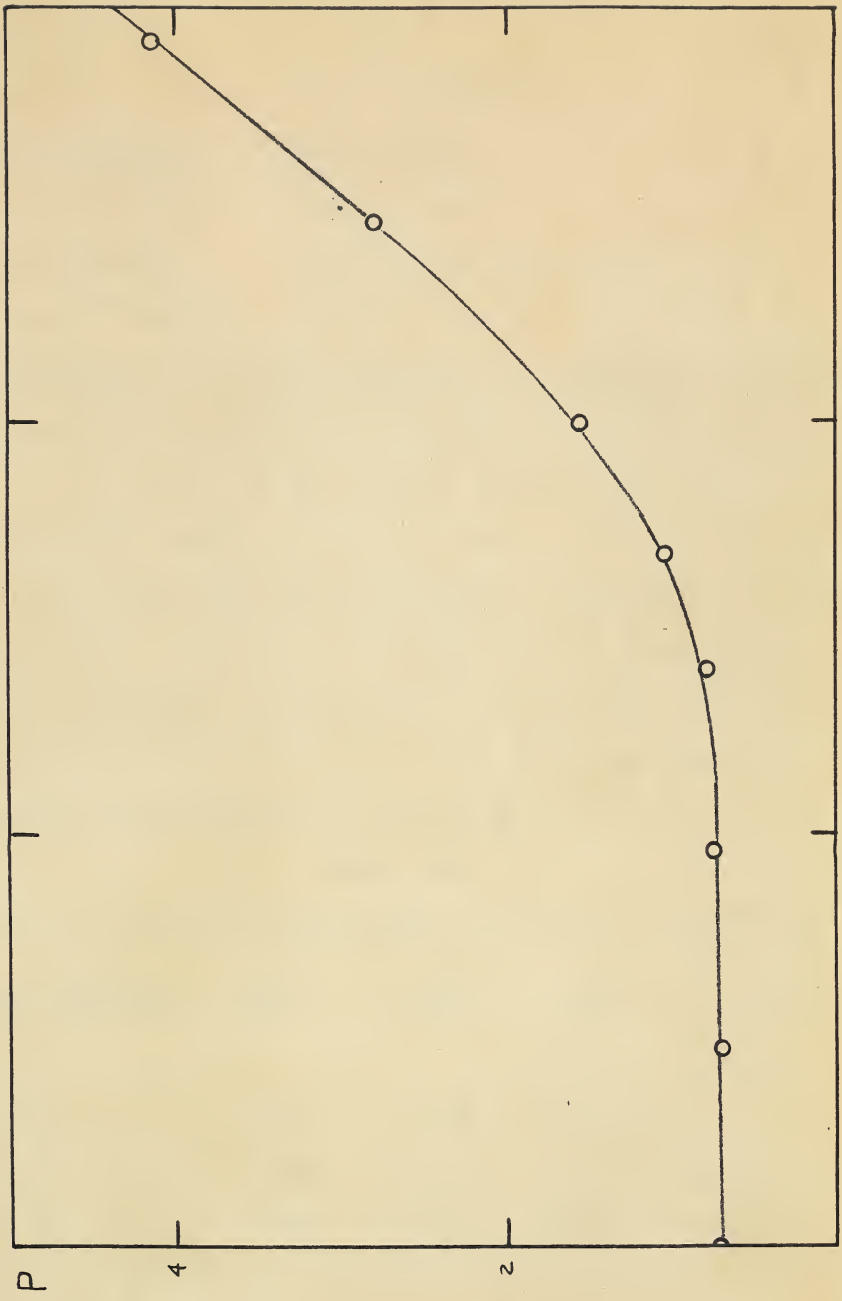

Figure 9 Vapour Pressure - Composition Diagram (at -78.9°C).

Table VIII

Temperature Baths Used

Substance	Type	Temperature
Methanol	Freezing Mixture	-97.8°C
Dry Ice-Ethanol	Sublimation	-78.9°C
Dry Ice-Acetone	Sublimation	-78.9°C
Chlorobenzene	Freezing Mixture	-45.2°C
o-dichlorobenzene	Freezing Mixture	-17.6°C

MEASUREMENT OF VAPOUR PRESSURE OF AN EQUIMOLAR MIXTURE OF ETHER AND HYDROGEN CHLORIDE IN AN INERT SOLVENT

Into a large weighed sample of n-heptane was introduced a small amount of ether. To this was added a nearly equal but smaller amount of hydrogen chloride. The vapour pressure of this mixture was measured as small increments of hydrogen chloride were added to bring the mixture up to and then past equimolarity. The data are tabulated in Table X.

Table IX

Vapour Pressure-Temperature at Constant Composition

$\frac{HCl\ (mmoles)}{Et_2O\ (mmoles)}$	P (mm.) -98°	P (mm.) -79°	P (mm.) -45°	P (mm.) -18°
0.10			12.55	74.35
0.14	0.10	0.95	10.55	
0.20	0.25	1.15	10.70	68.20
0.25	0.35	1.15	10.45	66.15

$\frac{HCl\ (mmoles)}{Et_2O\ (mmoles)}$	P (mm.) -98°	P (mm.) -79°	P (mm.) -45°	P (mm.) -18°
0.33	0.45	1.10	10.25	63.55
0.36			10.65	63.10
0.45	0.30	1.00		61.25
0.49				63.05[1]
0.50	0.15	0.70	10.60	61.45
0.62	0.25	0.70	11.10	70.35
0.74	0.25	0.75	13.90	80.30
0.85	0.15	0.80	19.60[1]	108.65[1]
0.89			18.45	88.00[2]
0.92	0.20	1.05	19.35	108.10
1.00	0.25	1.55	26.70	126.65
1.12	0.40	2.80	42.60	170.85
1.23	0.75	4.15	62.95	

[1] Temperature high, reading not plotted.

[2] Temperature low, reading not plotted.

Table X

Vapour Pressure of the 1:1 Complex in an Inert Solvent

Amount of n-heptane	40.8 mmoles
Amount of ether	2.41 mmoles
Temperatures used T_1	-76.7°C
T_2	-18.4°C

HCl (mmoles)	$\frac{\text{HCl mmoles}}{Et_2O \text{ mmoles}}$	P_1 (mm.)	P_2 (mm.)
2.14	0.89	1.90	92.05
2.37	0.99	2.75	107.90
2.66	1.11	5.45	123.30

Figure 10 Vapour Pressure - Composition Diagram (at -78.9 and -97.8°C).

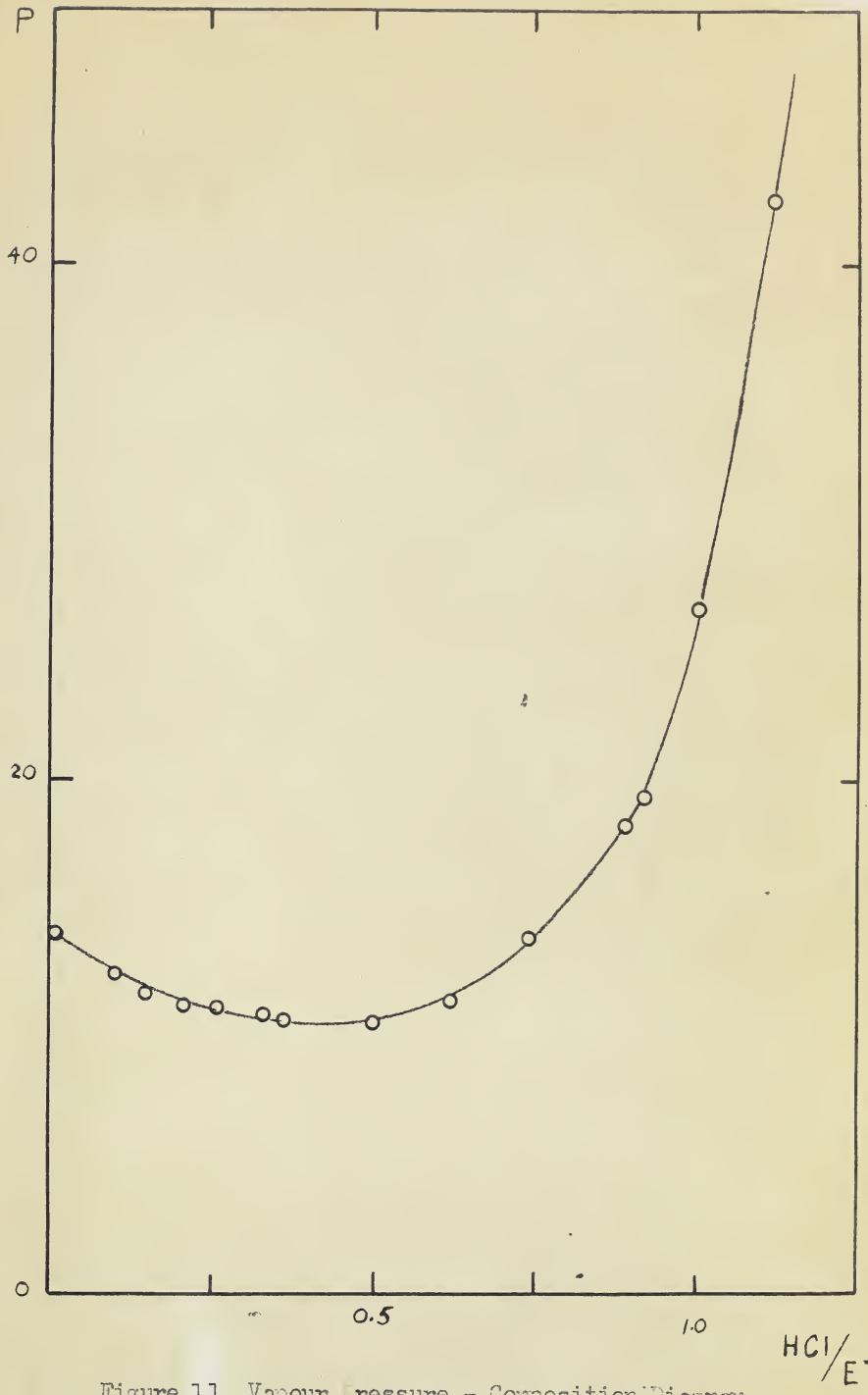

Figure 11 Vapour Pressure - Composition Diagram (at -45.2°C).

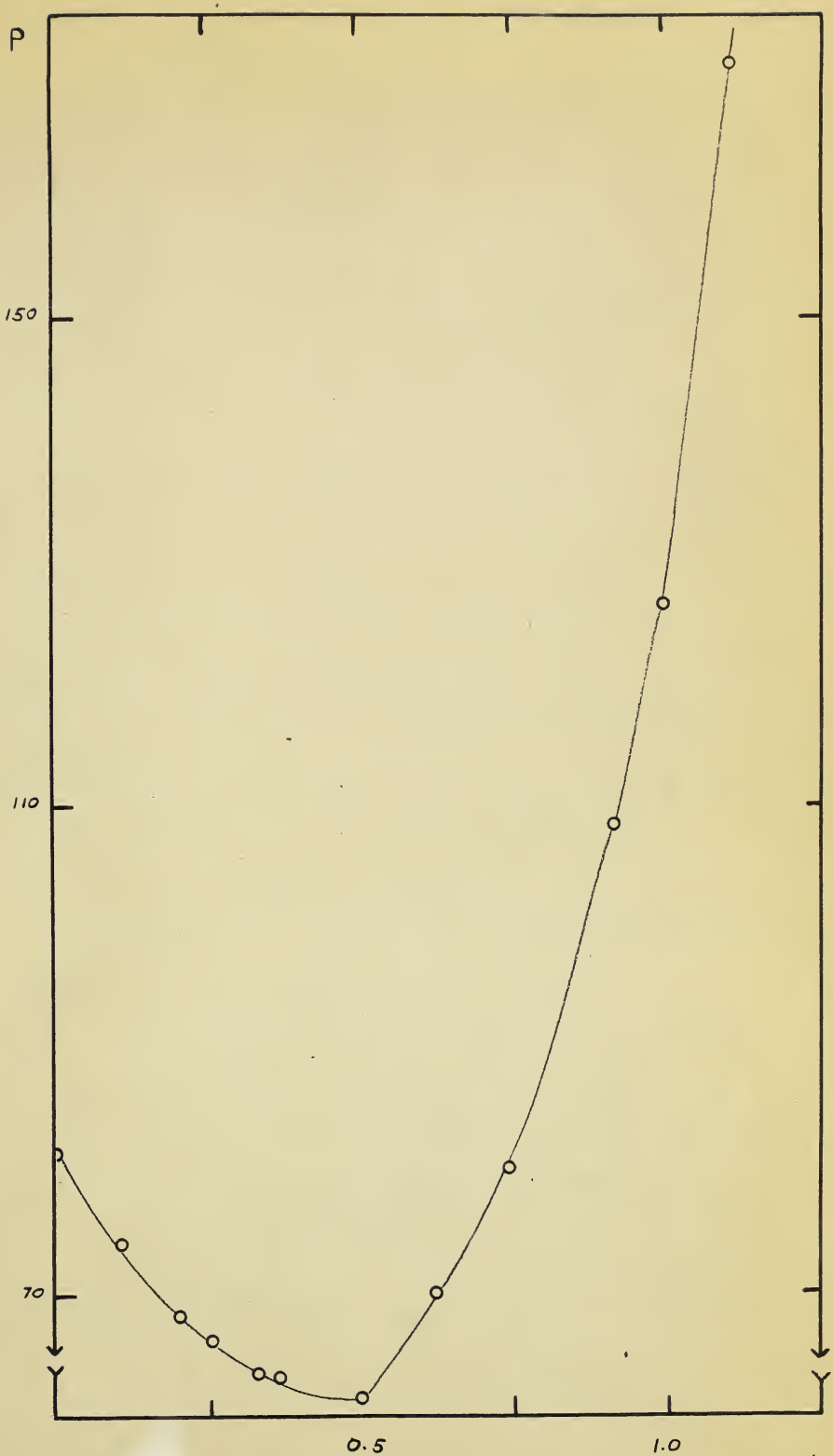

Figure 12 Vapour Pressure - Composition Diagram
(at - 17.6°C)

EVALUATION OF THE PHYSICAL EXISTENCE OF THE COMPLEXES FROM THE DATA

When the system: diethyl ether-hydrogen chloride was considered for further study, it was assumed from previous work, that the most probable complexes would be Et_2OHCl and $Et_2O(HCl)_2$. However, it was suspected from the discontinuous behavior of the vapour pressure-composition isotherms at lower temperatures, that some sort of complex was forming involving the components in the ratio of 2 molecules of ether per molecule of hydrogen chloride. In order to study the behaviour of the system and to ascertain which of these (or if all, in what ratio) species were present as complexes in solution, the experimental data had to be reduced into a more workable form. This could be achieved by subtracting the ether contribution from the composite curve, thus leaving a curve representing the free hydrogen chloride in equilibrium with the complex in solution.

To accomplish this separation, certain assumptions had to be made and then their validity tested.

ASSUMPTION 1 - All complexes between ether and hydrogen chloride exert a negligible vapour pressure. Thus the pressure curve represents only a composite of the partial pressures of ether and hydrogen chloride. We can use Raoult's law to resolve the curve.

$$P = \sum_{i=1}^{i} P_i^{\circ} \; x_i$$

where P is the observed pressure

P_i° is the vapour pressure of the pure i^{th} component, and x_i is the mole fraction of the i^{th} component in solution.

If we know the mole fraction of the free ether in solution, at any mole ratio, then we can calculate the pressure contribution of the ether to the resultant pressure of the system.

$$x_{Et_2O} = \frac{P_{Et_2O}}{P^\circ_{Et_2O}}$$

Knowing the contribution of ether, then the mole fraction of hydrogen chloride in solution can be calculated.

$$P_{HCl} = P_{Total} - P_{Et_2O}$$

$$x_{HCl} = P_{HCl} / P^\circ_{HCl}$$

The total mole fraction of complex in solution can now be calculated.

$$x_{complex} = 1 - x_{HCl} - x_{Et_2O}$$

However, the first problem that arises is that we do not know the mole fraction of ether left in solution. Hence we must assume the reaction taking place and calculate a theoretical value for the residual ether in solution.

ASSUMPTION 2 - The ether reacts with hydrogen chloride to form a 2:1 compound, $(Et_2O)_2HCl$ (which we shall henceforth denote as C_{21}), before further reaction with hydrogen chloride to form an equimolar compound.

The reaction in question is -

$$2\ Et_2O + HCl \rightleftarrows (Et_2O)_2HCl \qquad Reaction_{21}$$

The equilibrium constant for this reaction is given by -

$$K_{21} = \frac{x_{C_{21}}}{x_{HCl} \left(x_{Et_2O}\right)^2}$$

If the amount of ether originally present is $(Et_2O)_o$, and if Assumption 2 is valid, then the amount of ether left after the formation of complex C_{21} is - $(Et_2O)_o$ - $2(Et_2O)_2HCl$ and the mole fraction of free ether is -

$$x_{Et_2O} = \frac{(Et_2O)_o - 2\ (Et_2O)_2HCl}{(Et_2O)_o - 2\ (Et_2O)_2HCl + (Et_2O)_2HCl}$$

The pressures exhibited by the system indicate that the complexes are little dissociated. Thus, we can assume, with only a small error, that $HCl_{total} = HCl_{complexed}$.

Now we can reduce the expression for the mole fraction of free ether in solution, by substituting the value of HCl (complexed) for the value of complex C_{21}.

$$x_{Et_2O} = \frac{(Et_2O)_o - 2HCl}{(Et_2O)_o - HCl}$$

Since it is also possible to calculate the mole fractions of free hydrogen chloride and complex C_{21}, values for K_{21} can then be calculated. These data are given for -17.6 and -45.2°C., in Tables XI and XIII. They are plotted in Figures 13 and 14. The calculations of values for K_{21} are given in Tables XII and XIV.

Table XI

Separation of the Vapour Pressure Curve into Components by Assumption 2 (at -17.6°C)

$\frac{HCl\ (mmoles)}{Et_2O\ (mmoles)}$	P_{total}	x_{Et_2O}	P_{HCl}
0.10	74.35	0.90	∿ 0.00
0.20	68.20	0.75	6.95
0.25	66.15	0.66	12.95
0.33	63.55	0.51	21.95
0.36	63.10	0.44	27.45
0.48	61.25	0.07	55.45
0.50	61.45	∿ 0.00	61.45

P°_{HCl} = 16.1 atm.[31]

$P^\circ_{Et_2O}$ = 82.0 mm.

Table XII

Calculation of K_{21} by Assumption 2 (at -17.6°C)

$\frac{HCl\ (mmoles)}{Et_2O\ (mmoles}$	$x_{HCl} \cdot 10^{-3}$	$x_{C_{21}}$	$K_{21} \cdot 10^{3}$
0.10	~ 0.00	0.04	0.012
0.20	5.76	0.25	0.75
0.33	1.82	0.49	1.05
0.36	2.27	0.56	1.31
0.48	4.59	0.92	8.84
0.50	5.02	0.99	~ 195,000

Table XIII

Separation of the Vapour Pressure Curve into Components by Assumption 2 (at -45.2°C)

$\frac{HCl\ (mmoles}{Et_2O\ (mmoles)}$	P_{total}	x_{Et_2O}	P_{HCl}
0.14	11.55	0.83	~ 0.00
0.25	10.45	0.66	1.15
0.33	10.25	0.51	3.10
0.45	10.60	0.18	8.15
0.50	10.60	~ 0.00	10.60

P°_{HCl}=6.11 atm.[31]

$P^{\circ}_{Et_2O}$ =13.65 mm.

Table XIV

Calculation of K_{21} using Assumption 2(at -45.2°C)

$\frac{HCl\ (mmoles)}{Et_2O\ (mmoles)}$	$x_{HCl} \cdot 10^{-3}$	$x_{C_{21}}$	$K_{21} \cdot 10^{4}$
0.25	0.259	0.34	0.30
0.33	0.672	0.49	0.28
0.45	1.75	0.82	1.5
0.50	2.29	0.99	~ 2,100.

It is now evident that Assumption 2 does not yield a constant equilibrium constant, so it must not be completely valid.

ASSUMPTION 3 - The ether reacts with the hydrogen chloride in equimolar proportions to form the compound Et_2OHCl by the reaction -

$$Et_2O + HCl \rightleftarrows Et_2OHCl \qquad \text{Reaction 10}$$

The equilibrium constant K_{10} is given by -

$$K_{10} = \frac{{}^{x}C_{11}}{{}^{x}_{HCl} \; {}^{x}_{Et_2O}}$$

Following a similar procedure as before to evaluate the mole fraction of ether, we get -

$${}^{x}_{Et_2O} = \frac{(Et_2O)_o - Et_2OHCl}{(Et_2O)_o - Et_2OHCl + Et_2OHCl}$$

$$= \frac{(Et_2O)_o - HCl}{(Et_2O)_o}$$

The results of the calculations giving the hydrogen chloride pressure are given in Tables XV and XVII, and the data from these Tables are plotted along with the previous curves (obtained from Tables XI and XIII) in figures 13 and 14. The calculations of K_{10} values are given in Tables XVI and XVIII.

Table XV

Separation of the Vapour Pressure Curve into Components by Assumption 3 (at -17.6°C)

$\frac{HCl\ (mmoles)}{Et_2O\ (mmoles)}$	P total	x Et_2O	P HCl
0.00	82.00	1.00	0.00
0.20	68.20	0.80	2.70
0.33	63.10	0.67	8.15
0.50	61.45	0.50	20.80
0.74	80.30	0.021	58.55
1.00	126.7	0.011	126.6

Table XVI

Calculation of K_{10} using Assumption 3 (at -16.6°C)

$\frac{HCl\ (mmoles)}{Et_2O\ (mmoles)}$	$x_{HCl} \cdot 10^{-3}$	$x_{C_{11}}$	$K_{10} \cdot 10^3$
0.20	0.22	0.20	1.13
0.33	6.76	0.30	0.73
0.50	1.72	0.50	0.59
0.74	5.38	0.72	0.51
1.00	13.8	0.98	3.50

Table XVII

Separation of the Vapour Pressure Curve into Components by Assumption 3 (at -45.2°C)

$\frac{HCl\ (mmoles)}{Et_2O\ (mmoles)}$	P total	x Et_2O	P HCl
0.25	10.45	0.75	∿ 0.00
0.33	10.25	0.67	0.80
0.50	10.60	0.50	3.60
0.74	13.90	0.27	16.15
1.00	26.70	∿ 0.00	26.70

Table XVIII

Calculation of K_{10} using Assumption 3 (at -45.2°C)

$\frac{HCl\ (mmoles)}{Et_2O\ (mmoles)}$	x HCl . 10^{-4}	x C_{11}	K_{10} . 10^3
0.33	1.73	0.33	0.28
0.50	7.75	0.50	1.30
0.74	21.9	0.74	1.26
1.00	57.6	0.98	∿ 8.33

These values for K_{10} although better than those for K_{21} (by Assumption 2) are not sufficiently constant.

ASSUMPTION 4 - The two complexes C_{11} and C_{21} exist simultaneously in solution in the following way -

$$2\ Et_2O + HCl \rightleftarrows (Et_2O)_2HCl \qquad \text{Reaction 21}$$

$$(Et_2O)_2HCl + HCl \rightleftarrows 2\ Et_2OHCl \qquad \text{Reaction 11}$$

$$K_{12} = \frac{{}^{x}C_{21}}{{}^{x}_{HCl}\,({}^{x}_{Et_2O})^2} \qquad K_{11} = \frac{({}^{x}_{C_{11}})^2}{{}^{x}_{C_{21}}\;{}^{x}_{HCl}}$$

$$K_{11} \cdot K_{21} = \frac{({}^{x}_{C_{11}})^2}{({}^{x}_{HCl})^2\;({}^{x}_{Et_2O})^2} = K_{10}^{\,2}$$

There must also exist a relationship such that -

$$K_{11} / K_{21} = N^2 \text{ (a constant) AT ANY ONE TEMPERATURE)}$$

So that

$$\frac{{}^{x}C_{11}\;\;{}^{x}Et_2O}{{}^{x}C_{21}} = N$$

ASSUMPTION 5 - The amount of higher complex formation (e.g. $Et_2O(HCl)_{2+}$) can be neglected. In any case, the formation of higher complexes requires the attachment of a second proton to any oxygen already co-ordinated with one proton (therefore one with lessened basisity), so that the order of magnitude of the equilibrium constants of higher complexes should be much less than those of K_{10}, K_{11}, or K_{12}. This assumption may not be valid at the lower temperatures used in this study.

ASSUMPTION 6 - The true pressure curve for hydrogen chloride is given by some curve, consisting of some combination of those curves given by Assumptions 2 and 3.

In this case -

$$x_{Et_2O} = \frac{(Et_2O)_o - 2a(Et_2O)_2HCl - b(Et_2OHCl)}{(Et_2O)_o - 2a(Et_2O)_2HCl - bEt_2OHCl + a(Et_2O)_2HCl + bEt_2OHCl}$$

Where a moles of C_{21} are formed per mole of HCl added, and b moles of C_{11} are also formed per mole of HCl added -

Again using -

$$a\ (Et_2O)_2Hcl = a\ HCl$$

and $$b\ (Et_2OHCl) = b\ HCl$$

we get -

$$x_{Et_2O} = \frac{(Et_2O)_o - (2a + b)\ HCl}{(Et_2O)_o - a\ HCl}$$

Unfortunately this method of arriving at the true mole fraction of ether present for the composite situation, can not be used in our case since we do not have a method of evaluating the factors a and b from our data.

It was found that in our case the most ready solution of the problem was to assume a value of K_{10} (K'_{10}) at each temperature, and attempt to construct a curve which would at all points satisfy K_{10}, K_{11}, and K_{12}. This would at the same time give a constant ratio $K_{11}/K_{12} = N$. Since only approximate magnitudes of N could be arrived at from the data, the N values were

chosen such that -

$$2\Delta H_{10} = \Delta H_{21} + \Delta H_{11}$$

The values of ΔH were arrived at by utilizing the Van't Hoff isochor.

$$\frac{d \ln k}{d T} = \frac{\Delta H}{R T^2}$$

This is a restatement of one of the conditions of Assumption 4.

From the results using Assumptions 2 and 3, it seems apparent that the values of K_{10} are more consistant at both temperatures than those of K_{21}. At -18° the values of K_{10} are much more nearly constant than those of K_{21}. Hence, it should be apparent that Assumption 3 is closer to being valid than is Assumption 2. This menas the value of K_{11} is almost as large as that for K_{21}.

We can thus, using Assumption 3, evaluate K_{10} at various points around equimolarity and from this evaluation arrive at an approximation to the true value of K_{10}.

Table XIX

Calculation of K'_{10} using Assumption 3 (-17.6°C)

$\frac{HCl \text{ (mmoles)}}{Et_2O \text{ (mmoles)}}$	x $.10^{-2}$ HCl	x Et_2O	$K_{10} .10^3$
0.85	0.70	0.15	0.80
0.92	0.84	0.078	1.4
1.00	1.38	0.020	3.5
1.12	1.41	0.014	5.0

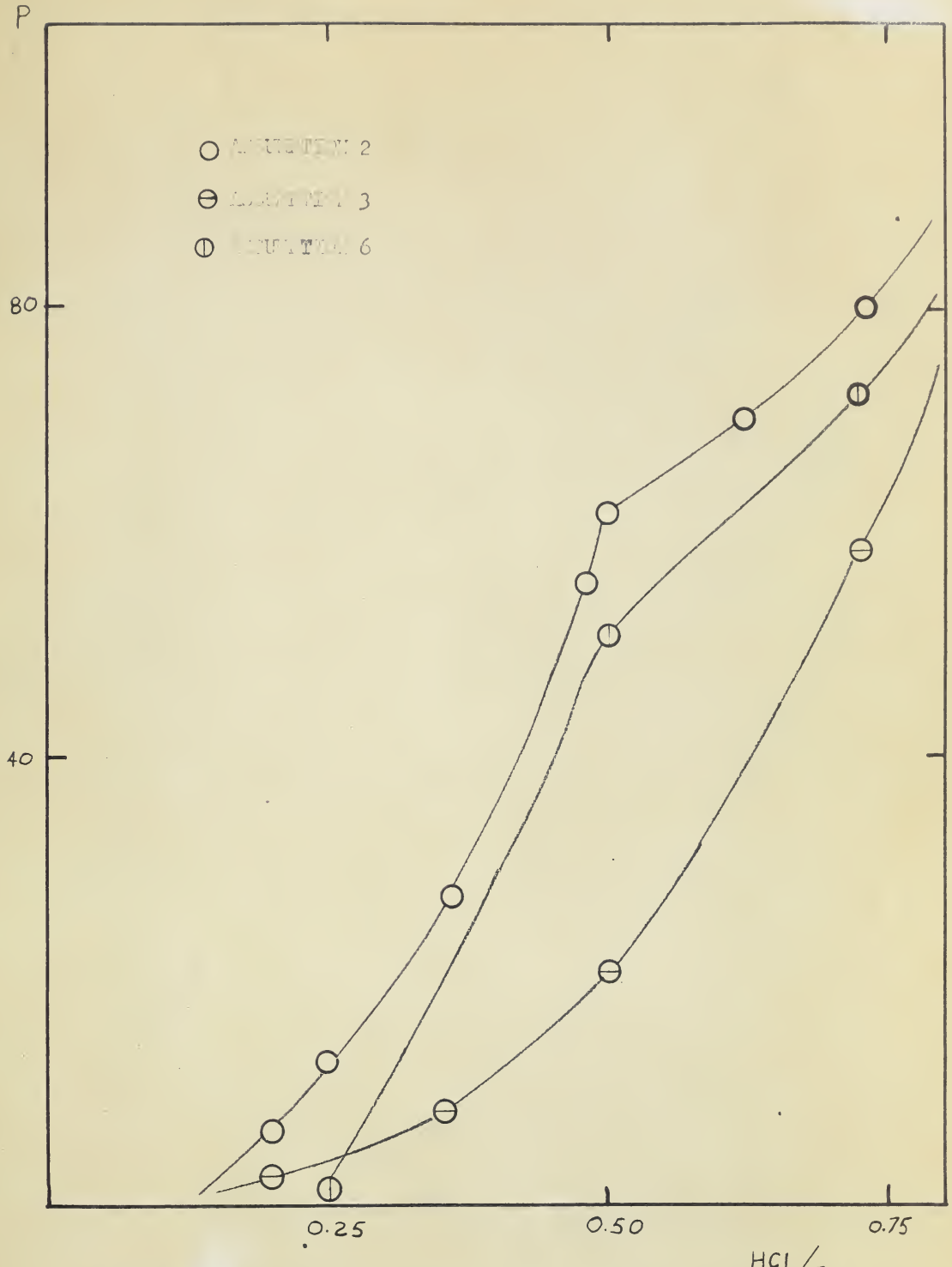

Figure 13 - Hydrogen Chloride Pressure - Composition Diagram (at -17.6°C).

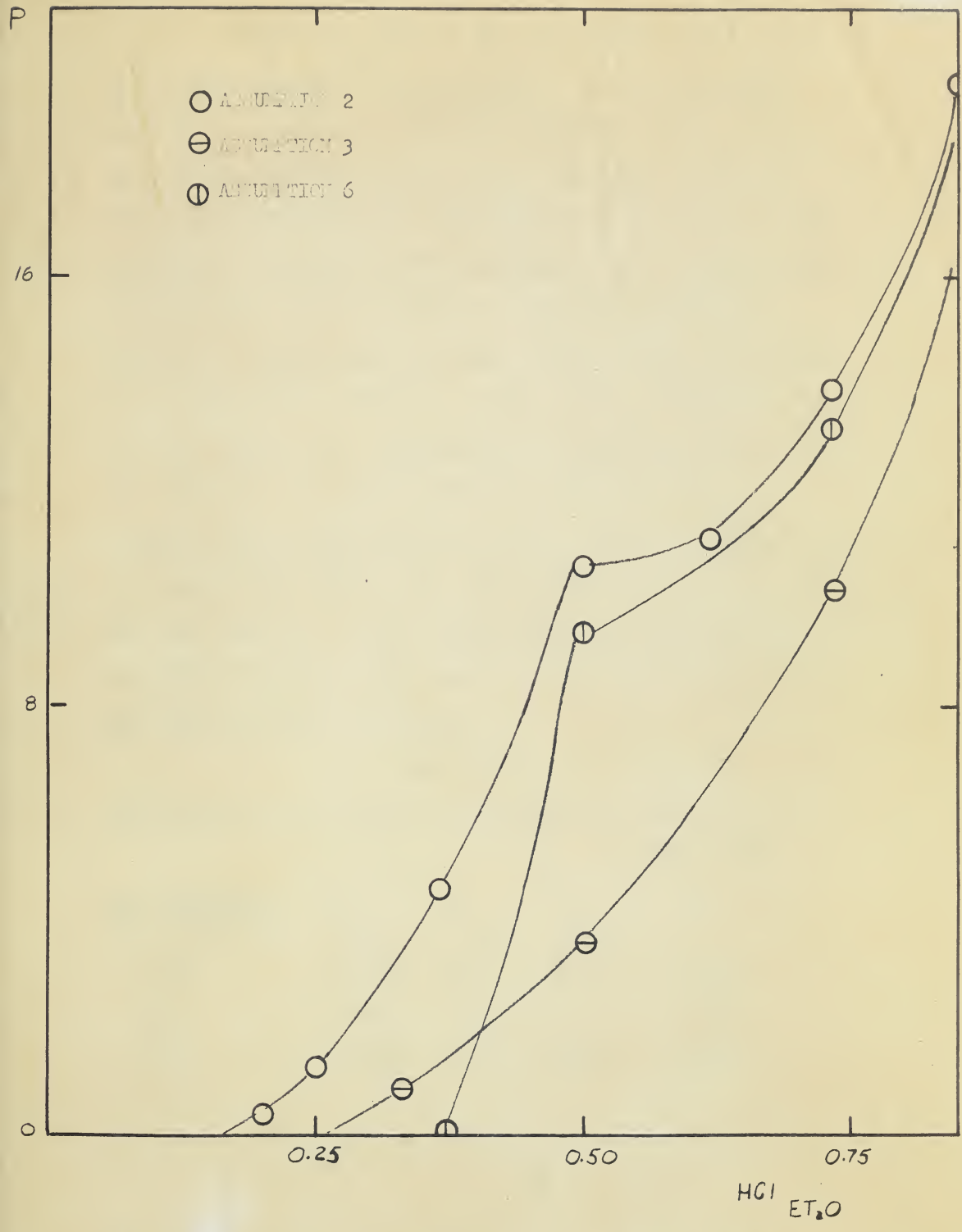

Figure 14 Hydrogen Chloride Pressure - Composition Diagram (at -45.2°C).

These K_{10} values are not constant even over this small range of compositions. This is probably because no correction for the formation of C_{21} or any enhancement of the solubility of hydrogen chloride above equimolarity as a consequence of a change in the dielectric constant of the medium as the concentration of the polar diethyl hydronium chloride increases. However, a reasonably accurate value of K_{10} can probably be arrived at by choosing a value of K_{10} somewhere close to, but lower than, equimolarity. The point chosen was one near the inflection point of the curve (K_{eq} vs. composition) as K_{eq} began to rise sharply as equimolarity was approached (fig. 15). The chosen value of K_{10} (K'_{10}) for -18° was $1.4 \cdot 10^3$. This value was then applied to the other points on the curve and best fit values of N, K_{21} and K_{11} were determined.

Table XX

Calculation of N values by Assumption 6 (at -17.6°C)

$K'_{10} = 1.40 \cdot 10^3$

$\frac{HCl\ (mmoles)}{Et_2O\ (mmoles)}$	P Et_2O	x C_{11}	x C_{21}	N
0.33	62.35	0.11	0.13	0.79
0.50	10.45	0.75	0.12	0.80
0.75	8.20	0.79	0.10	0.79

$\overline{N} = 0.79$

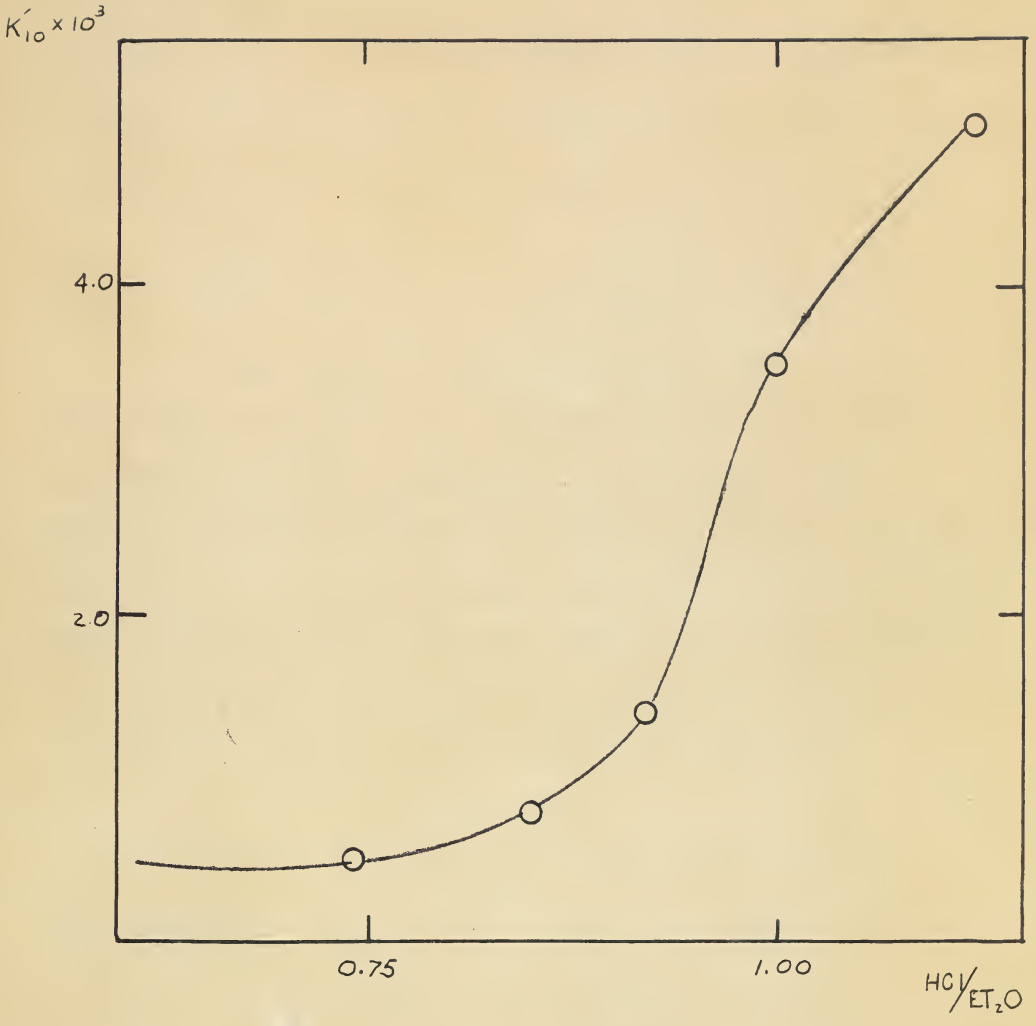

Figure 15 K_{10} vs. Composition using Assumption 3 (at -17.6°C).

Table XXI

Calculation of K_{21} and K_{11} values from N (at -17.6°C)

$\frac{HCl\ (mmoles)}{Et_2O\ (mmoles)}$	$K_{21} \cdot 10^3$	$K_{11} \cdot 10^3$
0.33	1.58	1.25
0.50	1.59	1.26
0.75	1.58	1.24

$\overline{K}_{21} = 1.58 \cdot 10^3$ $\overline{K}_{11} = 1.25 \cdot 10^3$

The values of K_{10} at -45° were more constant than those of K_{21} but not as much so as at -18°, hence the value of N was considered to be much less than before. This meant that the complex C_{21} would interfere more in the determination of a good approximation of K_{10}. Thus the value vhosen for -45° should be chosen closer to equimolarity than before, but as before, the point should fall close to the inflection of the curve.

Table XXII

Determination of K'_{10} by Assumption 3 (at -45.2°C)

$\frac{HCl\ (mmoles)}{Et_2O\ (mmoles)}$	$x_{HCl} \cdot 10^{-3}$	x_{Et_2O}	$K_{10} \cdot 10^3$
0.85	2.97	0.151	1.9
0.92	3.94	0.78	3.0
1.00	5.76	0.20	8.3
1.12	9.20	0.014	7.6

$K'_{10} = 5.0 \cdot 10^3$

This value was applied to the curve as before, and the best fit value of N, satisfying Assumption 4, was determined.

Table XXIII

Calculation of N values by Assumption 6 (at -45.2°C)

$\frac{HCl\ (mmoles)}{Et_2O\ (mmoles)}$	P Et_2O	x C_{11}	x C_{21}	N
0.36	10.58	0.057	0.193	0.22
0.50	1.21	0.87	0.039	0.19
0.74	0.75	0.75	0.19	0.21

The value of $\overline{N}$ arrived at was 0.21, which is about that expected from our original premise; that K_{21} was greater in relation to K_{11} than before. Values of K_{11} and K_{21} were easily derived from this N value.

Table XXIV

Calculation of values for K_{21} and K_{11} from N (at -45.2°C)

$\frac{HCl\ (mmoles)}{Et_2O\ (mmoles)}$	$K_{21} \cdot 10^4$	$K_{11} \cdot 10^3$
0.36	2.34	1.06
0.50	2.34	1.07
0.74	2.28	1.09

$\overline{K}_{21} = 2.32 \cdot 10^4$ $\overline{K}_{11} = 1.07 \cdot 10^3$

Since at lower temperatures, Assumption 5 does not necessarily hold, the values for the equilibrium constants can not be determined directly. Thus values

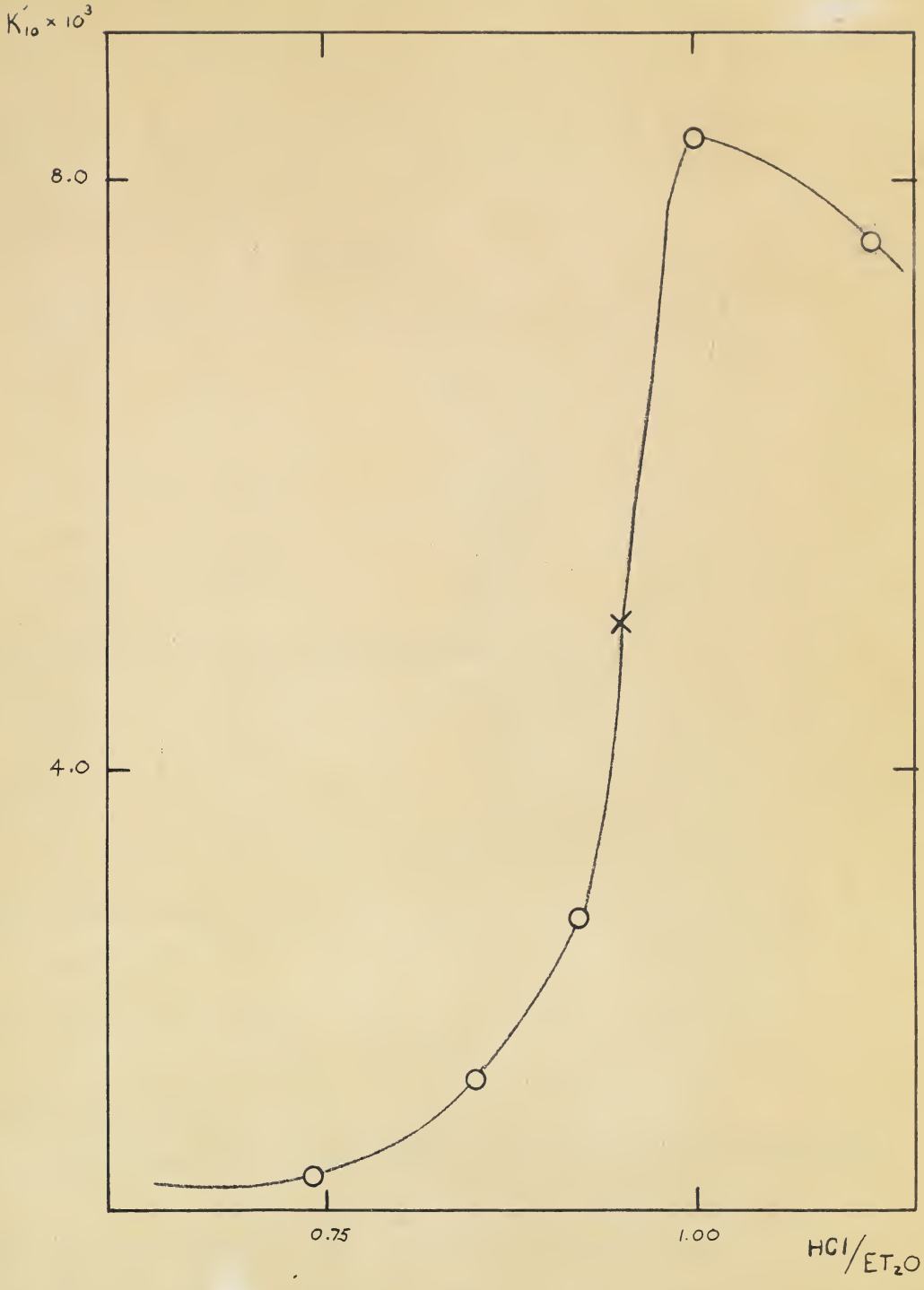

Figure 16. K_{10} vs. Composition using Assumption 3 (at -45.2°C).

obtained at -18° and -45°C. were extrapolated to obtain values for the lower temperature equilibrium constants (Fig. 17). The results of the extrapolation are given below in Table XXV.

Table XXV

Extrapolation of the Equilibrium Constant Values

T(°K)	$K_{10} \cdot 10^4$	$K_{11} \cdot 10^3$	$I_1 \cdot 10^4$
256.5	0.14	1.25	0.16
227.9	0.50	2.32	1.07
194.2	3.50	6.05	14.0
175.3	14.8	12.5	92.0

K_{10} values calculated from Assumption 3.

T(°K)	$K_{10} \cdot 10^4$
194.2	3.48
175.3	6.85

The close agreement of the calculated and extrapolated values for K_{10} is certainly fortuitous. In the calculations no allowance was made for C_{21}, which was certainly present. Also, no allowance was made for any formation of higher complexes (e.g. $Et_2O(HCl)_2$) which were probably present at these temperatures.

CALCULATION OF THE THERMODYNAMIC FUNCTIONS FOR THE COMPLEXES

Since the equilibrium constants K_{10}, K_{11}, and K_{21} have already been evaluated, the heats of association may now readily be calculated using the Van't

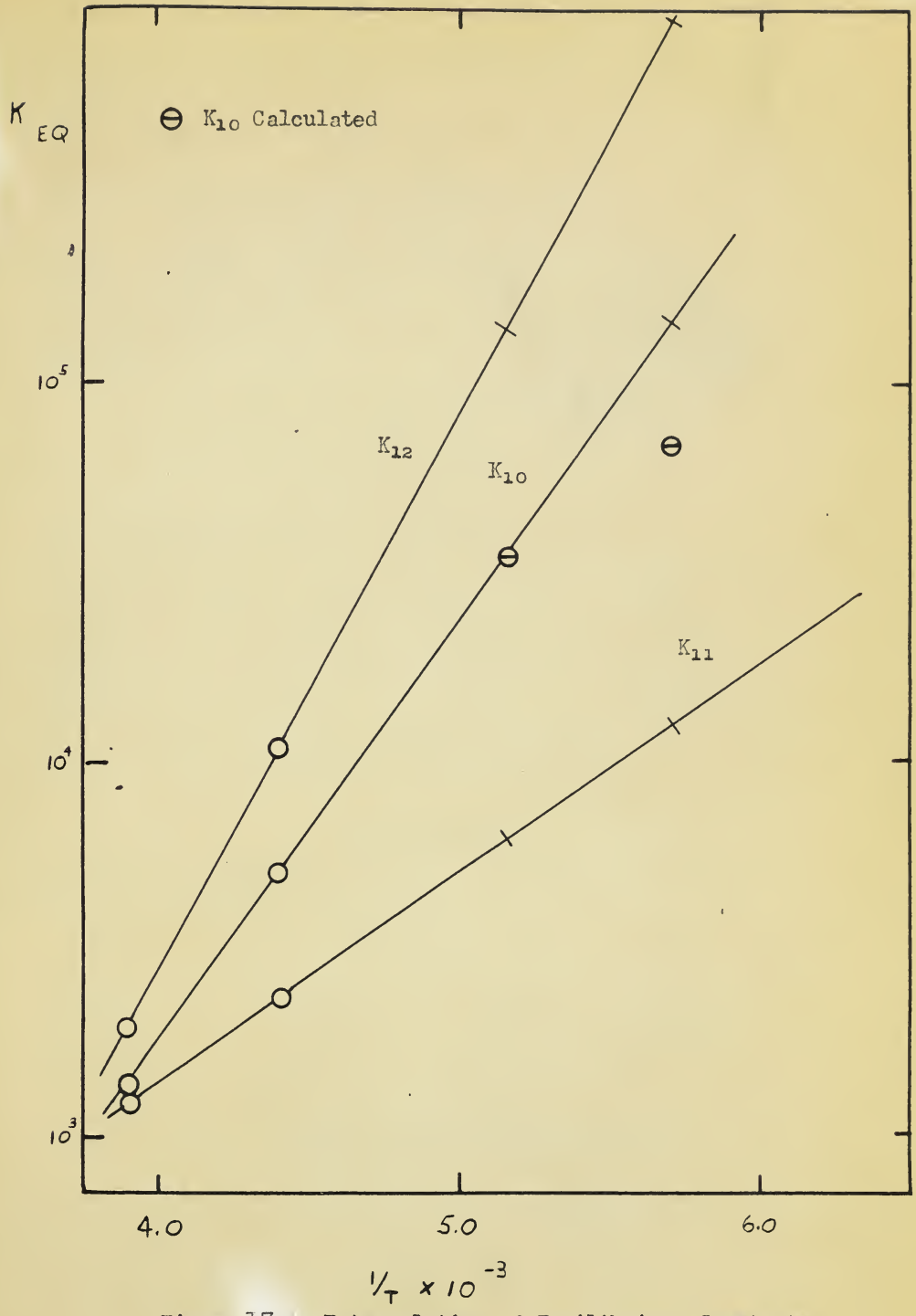

Figure 17 Extrapolation of Equilibrium Constants

Hoff isochor. The heats of association are given for the various equilibria in Tables XXVI, XXVII, and XXVIII.

Table XXVI

Heat of Association for Reaction 21

T(°K)	$1/T \cdot 10^{-3}$	$K_{21} \cdot 10^{3}$	log K
256.5	3.90	1.58	3.1987
227.9	4.39	10.7	4.0294

$\Delta H_{21} = -3.37$ kcal/mole.

Table XXVII

Heat of Association for Reaction 11.

T(°K)	$1/T \cdot 10^{-3}$	$K_{11} \cdot 10^{3}$	log K
256.5	3.90	1.25	3.0969
227.9	4.39	2.32	3.3655

$\Delta H_{11} = -1.09$ kcal/mole.

Table XXVIII

Heat of Association for Reaction 10.

T(°K)	$1/T \cdot 10^{-3}$	$K_{10} \cdot 10^{3}$	log K
256.5	3.90	1.40	3.1461
227.9	4.39	5.00	3.6990

$\Delta H_{10} = -2.25$ kcal/mole.

The free energy changes accompanying the formation of the various compounds are readily calculated from the equilibrium constants using the thermodynamic relationship -

$$\Delta F = - R T \ln K_{eq}$$

The free energy changes accompanying the formation of the various complexes are evaluated from the data and given in Tables XXIX, XXX, and XXXI.

Table XXIX

Free energy of Formation of Complex 21.

$K_{21} \cdot 10^3$	ln K	T(°K)	-ΔF(kcal/mole)
1.58	7.3652	256.5	3.75
10.7	9.2780	227.9	4.20
140.	11.8494	194.2	4.57
920.	13.7321	175.3	4.78

Table XXX

Free Energy of Conversion of Complex 21 to Complex 11.

$K_{11} \cdot 10^3$	ln K	T(°K)	-ΔF(kcal/mole)
1.25	7.1309	256.5	3.63
2.32	7.7498	227.9	3.51
6.05	8.7079	194.2	3.36
12.5	9.4334	175.3	3.29

Table XXXI

Free Energy of Formation of Complex 11.

$K_{10} \cdot 10^3$	ln K	T(°K)	-ΔF(kcal/mole)
1.40	7.2443	256.5	3.78
5.00	8.5172	227.9	3.86
35.0	10.4631	194.2	4.04
148.	11.9049	175.3	4.15

The entropy changes accompanying the formation of the various complexes can now be calculated using the thermodynamic relationship -

$$\Delta F = \Delta H - T \Delta S$$

The entropy changes are given for the various complexes in Tables XXXII, XXXIII, and XXXIV.

Table XXXII

Entropy Change Accompanying the Formation of Complex 21

-ΔF(kcal/mole)	-ΔH(kcal/mole)	T(°K)	+ΔS (eu.)
3.75	3.37	256.5	1.48
4.20	3.37	227.9	3.64
4.57	3.37	194.2	6.18
4.78	3.37	175.3	8.04

Table XXXIII

Entropy Change Accompanying the conversion of Complex 21 to Complex 11

-ΔF(kcal/mole)	-ΔH(kcal/mole)	T(°K)	+ΔS (eu.)
3.63	1.09	256.5	9.90
3.51	1.09	227.9	10.6
3.36	1.09	194.2	11.7
3.29	1.09	175.3	12.5

Table XXXIV

Entropy Change Accompanying the Formation of Complex 11

-ΔF(kcal/mole)	-ΔH(kcal/mole)	T(°K)	+ΔS (eu.)
3.78	2.25	256.5	5.97
3.86	2.25	227.9	7.06
4.04	2.25	194.2	9.73
4.15	2.25	175.3	10.8

CALCULATION OF THE VALUE FOR K_{10} IN AN INERT SOLVENT

Since in the liquid phase, Assumption 3 came closest to the actual physical situation occurring in the system, and since the solution data (in n-heptane) were only taken near equimolarity, the values for K_{10} were evaluated in a similar fashion to those for K'_{10} in the liquid phase. The data are tabulated in Tables XXXV and XXXVI for the two temperatures used, and their values are plotted in Figure 18.

Table XXXV

Evaluation of K_{10} in solution (at -18.4°C)

$\frac{HCl\ (mmoles)}{Et_2O\ (mmoles)}$	P_{total}	x_{Et_2O}	$x_{HCl} \cdot 10^{-3}$	K_{10}
0.89	92.05	0.079	7.41	95
0.99	107.9	0.017	9.22	355
1.11	123.3	0.015	10.5	353

$K'_{10} = 155$

Table XXXVI

Evaluation of K_{10} in solution (at -76.7°C)

$\frac{HCl\ (mmoles)}{Et_2O\ (mmoles)}$	P_{total}	x_{Et_2O}	$x_{HCl} \cdot 10^{-3}$	K_{10}
0.89	1.90	0.085	1.52	432
0.99	2.75	0.023	2.26	1,074
1.11	5.45	0.021	4.50	590

$K'_{10} = 740$

EVALUATION OF THE THERMODYNAMICS OF THE SYSTEM IN SOLUTION

The free energies, heats of association, and entropies accompanying the reaction were calculated. These data are Tabulated in Tables XXXVII, XXXVIII, and XXXIX respectively.

Table XXXVII

Free Energy Change Accompanying the formation of Complex 11 in Solution

K_{10}	ln K	T(°K)	-ΔF (kcal/mole)
155	5.0435	254.7	5.46
740	6.0633	196.4	2.58

Table XXXVIII

Heat of Association for Reaction 10 in Solution

T(°K)	$1/T \cdot 10^{-3}$	K_{10}	log K
254.7	3.93	155	2.1903
196.4	5.09	740	2.8692

$\Delta H = -1.16$ kcal/mole

Table XXXIX

Entropy Change Accompanying the Formation of Complex 11 in Solution

-ΔF(kcal/mole)	-ΔH(kcal/mole)	T(°K)	+ΔS (eu.)
5.46	1.16	254.7	16.8
2.58	1.16	196.4	7.23

COMPARISON OF THE SYSTEM IN THE GAS PHASE, IN THE LIQUID PHASE, AND IN SOLUTION

Maass and Russel[9] studied the system: diethyl ether - hydrogen chloride in the gas phase. Part of their data is used here for the purpose of comparison.

They obtained a value for K_{10} of $5 \cdot 10^3$ (at 50°C.) and a heat of association of -5.4 kcal/mole.

This data plus the data obtained for K_{10} and ΔH_{10} in the liquid phase and in solution are plotted together in Figure 18.

The heat of condensation of the system is -3.15 kcal/mole, and the heat of solution of the system in n-heptane is -1.09 kcal/mole.

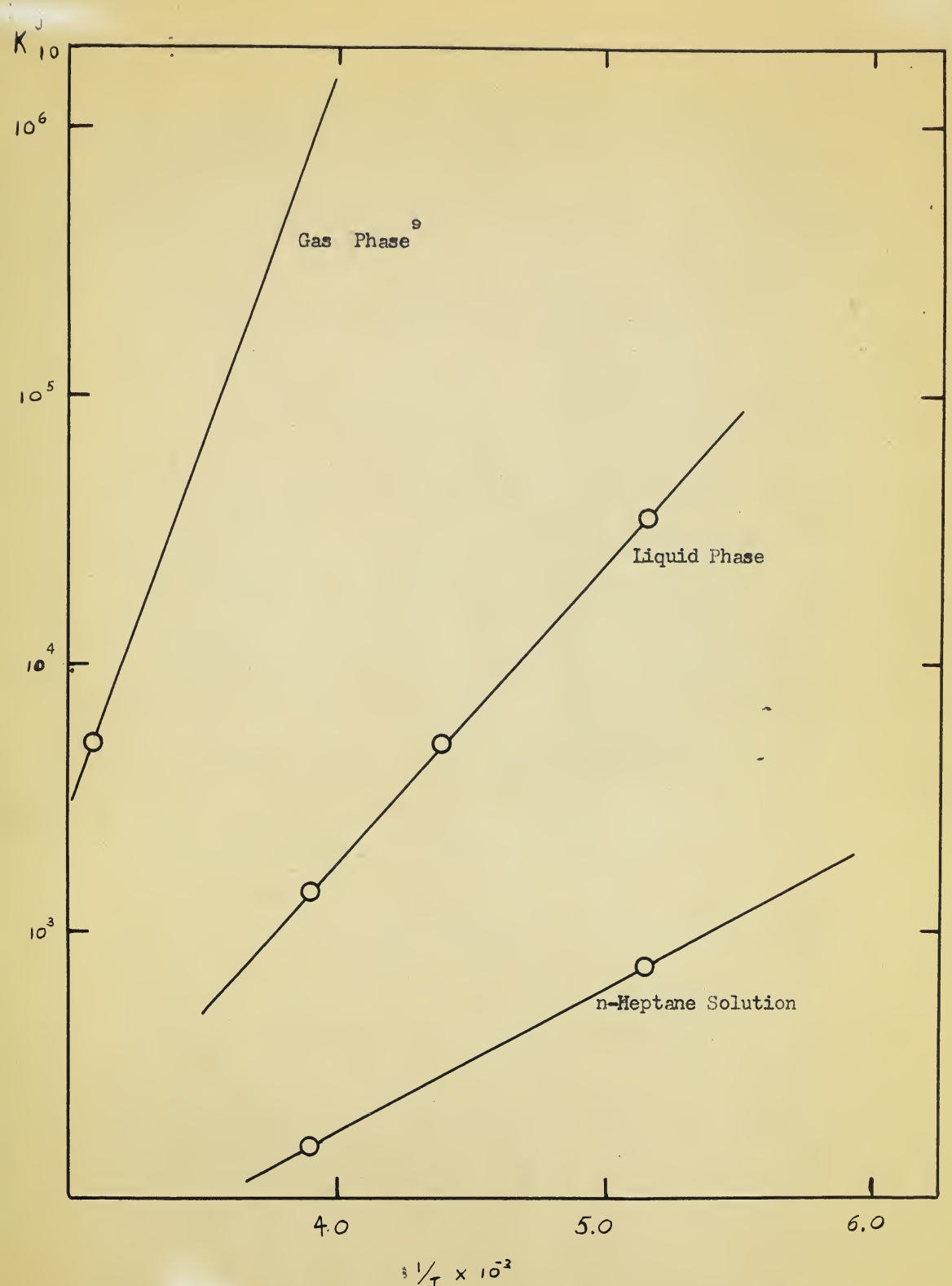

Figure 18 Comparison of ΔH values from K_{10} in Different Media

DISCUSSION

The vapour pressure-composition data indicate that marked interaction occurs between diethyl ether and hydrogen chloride, both in the liquid phase and in solution of the inert solvent n-heptane. Previous work has shown that the components interact readily in the gas phase[9] even at considerably higher temperatures. The components interact to form a colourless homogeneous solution containing complexes, which are not stable enough for isolation. However, their properties were investigated over a wide range of temperatures, and it was found that in the interval investigated, several complexes appeared to be important. The most important were those with the compositions: one molecule of ether per molecule of hydrogen chloride (1:1 complex) and two molecules of ether per molecule of hydrogen chloride (2:1 complex). It is possible that at the lower temperatures a third complex with two molecules of hydrogen chloride per molecule of ether (1:2 complex) was present.

Previous investigations of the system: diethyl ether-hydrogen chloride, have centered around the 1:1 complex. In solution, these studies have utilized such properties as freezing points[5,18], viscosity[14], and conductivity[14,16]. However, in the gas phase, vapour pressure studies have been undertaken[9]. In this study comparison was made between the measure-

ments made in the gas phase, in the pure liquid phase, and in solution with an inert solvent (heptane). The heat of association in the gas phase (-5.4 kcal/mole) was greater than in the liquid phase (-2.25 kcal/mole), which in turn was greater than in dilute solution (-1.16 kcal/mole). The disturbing factor is the order of the ΔH values between the three media. A possible explanation for the relative magnitudes of these ΔH values may be found in variation of the dielectric constants between the media under investigation. In the gas phase the value for dielectric constant is probably not too different from unity. However, in ether, the presence of equimolar amounts of polar hydrogen chloride may greatly enhance the value of dielectric constant for ether from the value for pure ether (5.72 at -40°; 8.14 at -100°). A dilute solution of ether in n-heptane should normally have a dielectric constant of close to 4, but the presence of the ether-hydrogen chloride complex and some free hydrogen chloride may enhance this value. If marked enhancement of the dielectric constant above the pure ether and pure heptane values occur in both the media, then the effect might be to alter the solubility of hydrogen chloride in these solutions. Hence the values obtained for the equilibrium constants would not be known exactly from our type of evaluation.

An approach to an explanation of the magnitude of difference in the ΔH values may be realized by considering the following cycle of reactions.

$$Et_2O_{(g)} + HCl_{(g)} \rightleftarrows Et_2OHCl_{(g)} \quad \Delta H = -5.4 \text{kcal/mole}^9 \qquad (1)$$

$$Et_2O_{(sol)} \rightleftarrows Et_2O_{(g)} \quad \Delta H \text{ is +ve.} \qquad (2)$$

$$HCl_{(sol)} \rightleftarrows HCl_{(g)} \quad \Delta H \text{ is +ve.} \qquad (3)$$

$$Et_2OHCl_{(g)} \rightleftarrows Et_2OHCl_{(sol)} \quad \Delta H \text{ is -ve} \qquad (4)$$

Equation one gives the interaction energy in the gas phase between the two components (ether and hydrogen chloride)[9]. Equation two gives the heat of vaporization of ether from a dilute solution of heptane. The value of ΔH will be positive. If the dielectric constant of the ether-heptane solution were enhanced, then the value of ΔH might conceivably be lowered. Similarly, equation three gives the heat of vapourization of hydrogen chloride from a dilute solution of heptane. Again the value of ΔH will be positive, however, here, the effect of an enhancement in the value of dielectric constant would be to raise the ΔH value. The fourth equation gives the heat of solution of the gaseous equimolar complex in heptane to form a dilute solution. In this case a negative ΔH value would be expected, and an enhancement of dielectric constant

of the resultant solution would tend to increase the ΔH value negatively. The sum of the equations (1, 2, 3, 4) should give the observed solution value of the heat of association between ether and hydrogen chloride (-1.16 kcal/mole). Measurements of the ΔH values for reactions two and three would be of use in evaluating a ΔH value for reaction four. This value may be of utmost importance in explaining the anamalous order of the ΔH values.

Another method of eliminating the uncertainty in the hydrogen chloride solubility would be to measure the solubility of hydrogen chloride in various media of measured dielectric constants and to attempt to make some correllation between the solubility (or the Henry's law constants) for these media and dielectric constant. The uncertainty of the solubility in solutions where complexing occurs could then be eliminated by directly measuring the dielectric constant of the media in which the complexing is occurring.

In a recent work,[25] Taube has made an evaluation of the entropy change occurring when a water molecule is removed from solution by association with an ion. The value that he attributes to this removal of one water molecule from solution by complexing is of the order of 6 eu. at room temperature.

From the value of entropy change occurring with the formation of the 1:1 ether-hydrogen chloride complex,

(+6 eu. at -17°), one would expect the nature of the association to be rather similar to the situation occurring when an ion is hydrated by a molecule of water from solution. It is in fact believed from the data, that the hydrogen chloride is strongly associated to the ether oxygen in the formation of the 1:1 complex.

The question of the structure of the 1:1 complex involves two extreme possibilities. The first of these was reported by West and Arthur[26, 27] from a study of the Raman spectra of hydrogen chloride in donor solvents of low dielectric constant. They postulate that the hydrogen chloride undergoes complete ionization in solution. This must come about as a result of the formation of unsymetrical hydrogen bonds between the solvent molecules, the acid proton, and the associated anion of the acid. In cases like diethyl ether, the oxygen-hydrogen bond may be sufficiently stronger than the hydrogen-chlorine bond, so that thermal agitation in the solution may completely sever the original acid bond, resulting in proton transfer to the solvent..

$$Et_2O + HCl \rightleftarrows Et_2OH^+ + Cl^-$$

It seems rather unlikely that an energy source of sufficient magnitude to promote charge separation in a medium of such a dielectric constant would be available to the system under the conditions of this study.

The second possibility is that reported by several investigators[2, 28] in which the interaction of hydrogen chloride with an active solvent merely results in a perturbation of the acid frequency which shifts it to longer wavelengths. The absence of the first harmonic of hydrogen chloride in solutions of donor solvents in both the Raman[26,27,29] and infrared[30] regions, showed the transfer theory to be the most likely. However, Gordy and Martin[28] have offered an explanation for the absence of the first harmonic. They have found that the presence of hydrogen bonding makes the potential energy function of the hydrogen chloride frequency so nearly a Hooke's law function that detection of the first harmonic is almost impossible. However, they have observed broad absorption corresponding to the second harmonic of the hydrogen chloride frequency, which makes the transfer theory appear incorrect.

The evidence offered in this study was insufficient to differentiate definitely between either of

the two theories. Actually only spectral evidence can be used for the purpose of deciding between the two. We do, however, have one point to add. It appears to be apparent from the previous discussion that the energetics of the reactions occurring do not allow complete charge transfer to occur. This fact is indeed verified when the entropy changes accompanying the reactions are considered. The case in which complete proton transfer had occurred should have less of an entropy change than the case where the proton is bound to both the ether oxygen and to its own chloride anion. So from our observed entropy changes, one would expect, at least in the liquid phase, that the complex is of such a nature that complete proton transfer does not take place.

The first complex to form in solution (ether) is the one containing two molecules of ether per molecule of hydrogen chloride (2:1). This complex does not appear to have previously been recorded in the literature. However, the effect of decreasing vapour pressure of an ether solution as a proton acid is added has been mentioned by Desmaroux, Dalmon, and Vandoni[21]. They studied the system: ether-nitric acid, and found that the vapour pressure isotherms gave a minimum at a mole ratio (HNO_3/Et_2O) of 0.5. This is consistent with our results with the system: ether-hydrogen chloride. It

is very possible that other investigators using other methods of investigation, have missed this 2:1 complex due to its similarity to the 1:1 complex with which it exists in equilibrium in solution.

We believe that the 2:1 compound has a structure which resembles the 1:1 complex; in other words, the hydrogen chloride is bound to one ether in a manner similar to the bonding in the 1:1 compound, but the second ether is held to the positive end of the resultant dipole through a loose linkage. The entropy values for this complex indicate that the first ether is not as tightly bound to the hydrogen chloride as it would be in the 1:1 complex, and the second ether is bound in such a way as to retain a great deal of its freedom.

The study of oxomium complexes using other members of the series (alcohols and water) would be of great value. Since the ether series of oxonium compounds presents the simplest case, most of the past studies have been done on ethers. The results obtained with the ethers have so far fallen into line with what little has been done on the other types of compounds in the oxonium series. However, future studies on all three types of compounds would be of great interest in unravelling the mysteries of this most interesting series.

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